



An overview on glycerol-free processes for the production of renewable liquid biofuels, applicable in diesel engines

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ABSTRACT

Biodiesel is a biofuel obtained from vegetable oils or animal fats by transesterification with methanol, so that it offers a very promising alternative respect to diesel fuel, since it is able to provide a suitable substitute for the fossil diesel in unmodified internal combustion engines, pure or in blends. However, a major barrier exists to consolidate this conventional biodiesel, as the more suitable biofuel for the replacement of fossil fuel. This drawback is related to the significant amount of glycerol obtained as a byproduct in the transesterification process, which exceeds at least 10% by weight of oil used as raw material. Thus, future widespread use of biofuels depends on developing new process technologies to produce high quality transportation fuels from biologically derived feedstocks, which avoid this key handicap. These new biofuels, like the biodiesel, need to be also compatible with the fossil fuel as well as with existing transportation infrastructures to be economically feasible. In this respect, various alternative methods are currently under development to convert vegetable oils into a high quality diesel fuel, fully compatible with petroleum derived diesel fuel but avoiding the existing glycerol glut. The present review aims to explore the current state of available technologies and recent information in research, production practices and engineering developed to produce alternative high-quality diesel fuel from vegetable oils, by hydrotreating of triglycerides in conventional oil refineries (green diesel) as well as those novel biofuels that integrate glycerol into their composition (Glicerol[®], DMC-Biod[®] and Ecodiesel[®]) and the respective technologies for their productions. These very recent biofuels obtained from oils and fats, seek to achieve greater atom efficiency (ideally 100%) because nor glycerol neither other byproduct is generated, avoiding any purification treatment, so that the overall production process of the biofuel is in large extension simplified.

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1. Introduction

The fossil fuel globally is currently the main primary source of energy and chemicals, however, together with the predictable demand to ensure a model of economic and social development worldwide accepted, it is found that its availability is becoming increasingly more limited, so it is also more accepted and assumed that the era of cheap and easily accessible fossil fuel is coming to its end. Thus, the high current oil consumption, about 90 million barrels of oil and liquid fuels were consumed per day (Fig. 1), will lead quickly to the depletion of fossil fuels. Thus, the International Energy Agency (IEA) has reported in the reference scenario that the world's primary energy need is projected to grow by 55% between 2005 and 2030, and near 2025, the world's demand for oil will shoot up to 60%, while production capacity could experiment relapsed to the levels of 1985 [1].

Therefore, there is a growing worldwide concern for environmental protection and for the conservation of non-renewable natural resources, so that is getting an unprecedented effort to evaluate alternatives (photovoltaic, wind, hydrogen and nuclear energy) [2,3] that allow a gradually replacing of natural gas, coal and fossil fuels in the field of electricity generation. But there is no such equivalent in transport sector, since vehicles capable of using fuel cells or electric motors cannot compete yet with the explosion or combustion engines, developed at the end of the nineteenth century and very refined over the next century. Especially, this is true in the aviation field [4]. Thus, in the short and medium term seems essential to obtain, economically and environmentally viable, technical alternatives to replace current fossil fuels. In this respect, it is urgent and needed to find a substitute that, being renewable, allows to current engines suitably work without any modifications [5]. In this respect, although, the diesel engine, invented by Rudolph Diesel over a century ago first ran on peanut oil, the current combustion engines are designed to run on hydrocarbon fuels derived from petroleum. Therefore, a substitute for diesel fuel from renewable source will need to have identical or closely similar properties. The most popular of the existing

technology to process vegetable oils or animal fats is based on the conversion of the triglycerides to fatty acids methyl esters (FAME) by a transesterification reaction with methanol. However, there are also several alternative routes to use vegetable oils or animal fats like a biofuel, including direct use of vegetable oil, microemulsions and emulsifications. Besides, some biofuels which can be termed "renewable diesel", because of its composition resembles that of fossil-derived fuel (petrodiesel), has been gaining attention in recent years. In this respect, several processes (cracking or pyrolysis, hydrodeoxygenation and hydrotreating) are being used to obtain these biofuels that resemble to petrodiesel [6–8]. In Fig. 2 are shown the main existing methods for the triglycerids transformation into applicable biofuels to diesel engines.

The major reason for not using a neat vegetable oil as fuel is its high viscosity, so that direct use of vegetable oil is not applicable to most of actual diesel engines, as the high viscosity would damage the engine. Vegetable oils exhibit viscosities ranging from 10 to 20 times higher than petroleum diesel fuel (usually in the range of 28–40 mm²/s). Thus, compression ignition engines that run on vegetable oils are susceptible to many problems because they are designed to run on petroleum diesel fuels. Some of the problems include: coking and trumpet formation on the injectors, to such an extent that fuel atomization does not occur properly or even prevented as a result of plugged orifices; carbon deposits; oil ring sticking; thickening, or lubricating problems due to gelling of the lubricating oil as a result of contamination by vegetable oils [9]. Besides, Biofuels obtained from microemulsion and thermal cracking methods would lead to incomplete combustion due to a low cetane number. Vegetable oil transesterification reduces the viscosity of the oil to a range (usually 4–5 mm²/s) closer to that of petrodiesel, so that it is at present the most common method for biodiesel production due to its simplicity and it has been widely studied and industrially used to convert vegetable oil into biodiesel [10,11]. In this connection, the production of biodiesel in recent years has become very important as potential alternative to partially fulfill the expected future energy demands in the transport sector [12,13].

Biodiesel, defined as fatty acids alkyl esters (FAAE) obtained by the transesterification of vegetable oils or animal fats with alcohols (e.g., methanol, ethanol), is a renewable and biodegradable fuel used as alternative energy source for diesel engines [14]. As a fuel, biodiesel has a comparable caloric value to petrodiesel, it has shown higher combustion efficiency, higher flash point, a higher cetane number and it possesses better lubricant efficiency. As far as the safety is concerned, the higher flash point makes biodiesel safer to handle, transport and store. The option of direct blending with petrodiesel as a fuel in compression-ignition engines at any blending ratio adds merit to biodiesel. The benefits of biofuels over traditional fuels also include greater energy security, reduced environmental impact, foreign exchange savings, and socioeconomic issues related to the rural sector. The use of waste oils and fats in biodiesel production also reduces many related environment complications.

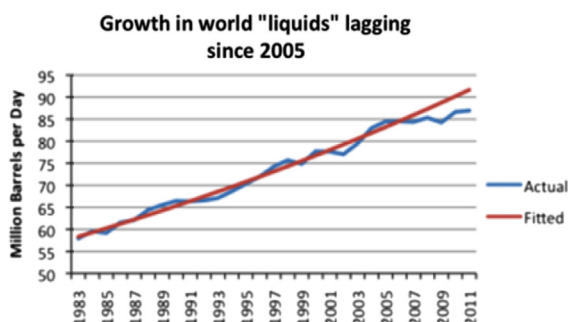


Fig. 1. Oil consumption in the past 20 years.
Source: IEA International petroleum monthly.

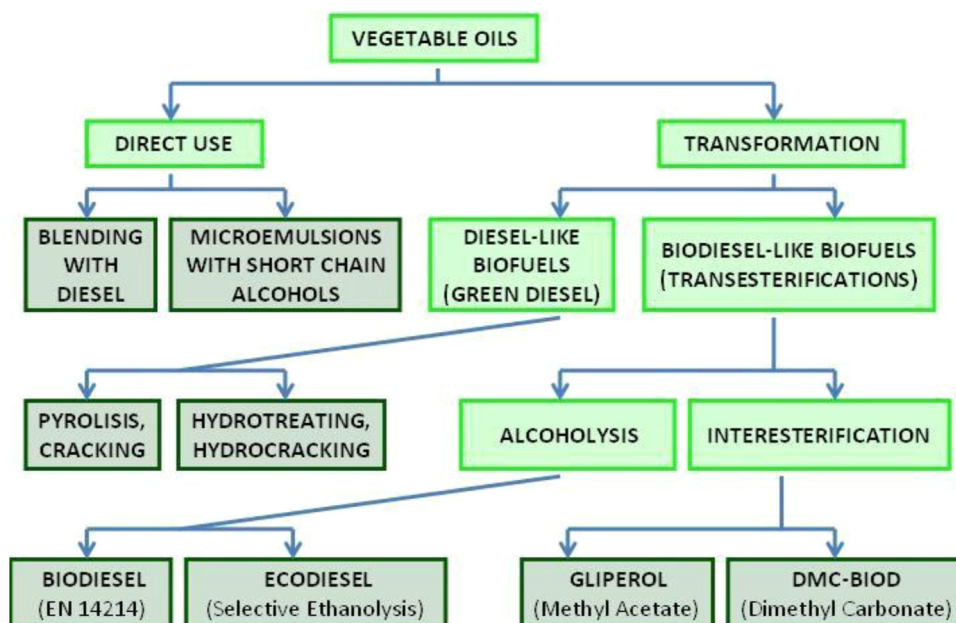


Fig. 2. Different methods for converting vegetable oils into biofuels

Several edible vegetable oils such as canola, palm, sunflower and coconut oil have been studied as feedstocks for biodiesel ("first generation") production. The main disadvantage concerning about biodiesel production from these feedstocks is the high price of combustible vegetable oils compared to that of fossil based diesel fuel. As a result, non-edible oils such as *Jatropha*, or waste cooking oils, are at present preferred for biodiesel production due to their low price. Besides, new generation biodiesel intends to derive raw material from algae and other renewable feedstock which will provide sustainability to the whole biodiesel production process necessary to adequately justify the biodiesel industry. For its fuel commercial use, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it conforms to international standards ASTM D 6751 and EN 14214. However, there are several technical challenges that still need to be overcome, to make profitable the biodiesel use. In this respect, there are not today insurmountable problems with biodiesel processing or with glycerol, however its production depends on the government subsidies or it is protected by national laws which oblige to use biodiesel in the country where the primary matter is produced.

As transesterification agent methanol is preferred due to its economical advantages and the transesterification reaction is generally catalyzed by acids [15,16] bases [17] and enzymes [18]. Although using enzymes leads to satisfying selectivities, the applicability of this method is economically limited by the high price of the enzymes, the very large reaction volumes and the reaction rates. When comparing the economy of enzymatically and chemically produced biodiesel, there are important factors to consider, such as yield, flexibility in feedstock, value of by-products, recovery costs for alcohol, as well as the cost and lifetime of the enzyme, and reaction times. The pros and cons of using lipases as biocatalysts comparatively to alkaline or acid catalysts for biodiesel production are related to the shorter reaction times and higher yields obtained, when chemical transesterification is applied. However, the drawbacks such as higher energy requirements, difficulties in the recovery of the catalyst and the glycerol, as the major potential environmental pollution, are the major disadvantages of the alkali or acid catalyzed processes. In general, lipases perform their catalytic activity under more gentle conditions and with a variety of triglyceride substrates, including waste

oils and fats with high levels of FFA. Furthermore, biodiesel separation and purification is much easier, resulting in a more environmentally friendly process. However, one of the bottlenecks for industrial application of lipases is the high cost of the biocatalysts. Some Immobilization methods are being introduced to improve lipase stability allowing for its repeated utilization [19].

However, the performance of homogenous basic catalysts in the transesterification process depends on the free fatty acid (FFA) or water content. Therefore content higher than 0.5 wt% FFA or 0.06 wt% water lead to the soap formation and to the reduction of the homogeneous basic catalyst activity. A solution for overcoming this problem is represented by the use homogeneous acid catalysts like H_2SO_4 or HNO_3 , because their performances are not strongly affected by the presence of free fatty acids or water and they can simultaneously catalyze both esterification and transesterification reactions. However, catalyzed reactions in acid medium are not as common as the reactions performed in basic medium because the reaction involve longer reaction times (up to 96 h) and higher alcohol:oil molar ratios (up to 150:1 mol). This reaction has also the advantage of not being affected by the presence of free fatty acids, since this process occurs in an esterification reaction and transesterification simultaneously. The most used catalyst is H_2SO_4 (sulfuric acid) and the concentration varies between 1 and 5% by weight. High concentrations of H_2SO_4 can promote further conversion, however an excess can also promote the formation of ethers by dehydration of alcohols. Furthermore, the amount of CaO required to neutralize the H_2SO_4 is increased by increasing the concentration of this acid in the reaction. Usually it is recommended a 30:1 (alcohol/oil) molar ratio to reach a conversion of about 98%, and a 6:1 M ratio for a conversion of about 87%. By using a high operating temperature can be achieve high conversion in less time. Furthermore, the acid catalysts are more corrosive than the basic ones limiting their industrial applications [20].

One of the main disadvantages with the use of homogeneous catalysts is the necessity of a neutralising and purification step of the reaction, a non-friendly environmental process, which produces high amounts of waste waters. The solution of these problems may be achieved by using heterogeneous catalysts, which can be easily recovered at the end of the reaction, and also

used for more reaction cycles without any pretreatment. In addition, heterogeneous catalysts are not corrosive. These catalysts are consisting of alkaline earth metals in the form of oxides and/or carbonates, in very various mixtures with each other. Among the most studied heterogeneous catalysts calcium oxide, either pure or supported on various materials (silica and alumina, etc.) has being proved highly recommended because of the possibility of reuse in the transesterification of soybean oil to produce biodiesel [21,22].

On the other hand, under supercritical conditions (temperature 350 to 400 °C and pressure > 65 MPa) with a very high alcohol:oil molar ratio (42:1), the reaction is completed in 4 min. Thus, in non-catalytic conditions but in supercritical methanol, the process involves operate under extreme conditions of temperature, and high pressures, what limits its application to industrial level, because of the costs of installation and operation are very high, with a very high energy consumption. Thus, although the results of this process may be adequate and faster, the building of an industrial plant with this technology can be actually very expensive [23–26]. Thus, the production of biodiesel at an industrial level is currently developed by using homogenous basic catalysts, such as NaOH, KOH or K and Na methoxides and always glycerol as main by-product is obtained.

2. Strengths, weaknesses and handicaps existing for the industrial fabrication of the FAME mixtures, that presently constitutes the conventional biodiesel

2.1. Industrial production of biodiesel

At present, most of biodiesel is produced by the transesterification of triglycerides with methanol using homogeneous alkaline catalyst to yield fatty acid methyl esters (FAMES) and glycerol. In order to shift the transesterification process to obtain the highest yield, the alcohol is used in excess, with respect to the stoichiometric molar amounts. Due to this, two immiscible phases are obtained, a higher stage where the ethyl esters (or methyl), namely biodiesel, and a lower phase where the glycerine is dissolved in the excess of alcohol used. Furthermore, a number of purification steps are needed in order to meet the stipulated qualities, which require longer reaction time and more operation staffs [27]. Moreover, there is a serious equipment corrosion caused by the acid–base and salt-containing waste water treatment, which increased the capital and operating costs, so that the overheads of biodiesel production remains higher than that of petroleum diesel fuel due to the feedstock and capital costs [28].

Homogeneous base catalysts are currently used because they result in adequate reaction rates and product yields. The reaction also proceeds at lower temperatures than the methanol boiling point and at normal pressure, thereby reducing the capital and operating costs associated with biodiesel production. However, homogeneous base catalysts have disadvantages such as equipment corrosion and the need to remove residual inorganic components from the biodiesel waste-water [29]. Furthermore,

in the presence of free fatty acids (FFA), alkali-hydroxides lead to soap formation, which reduces the FAME yield. In this respect, the process is far from being environmentally friendly as the final mixture needs to be separated, neutralised and thoroughly washed, generating a great amount of waste (e.g., salt residues, waste water), reducing at the same time the quality of the glycerol obtained as by-product. The catalyst cannot also be recycled. A consequence of these problems is the increase of biodiesel production costs [30].

Recently, scientific community has directed much attention toward innovative ways to lower costs in biodiesel fabrication. Thus, a continuous process is preferred for biodiesel industrial production, since it is more convenient and economical, so that several procedures have been investigated for use in continuous reactors, such as a plug flow reactor, reactive distillation column, and a microtube reactor, using either sodium methoxide or sodium hydroxide [31–33] as well as heterogeneous base catalysts [34,35]. However, most important drawbacks follow without solution in the industrial fabrication of biodiesel.

In this respect, an excess of methanol is normally utilized in this process in order to shift the equilibrium to the production of FAMES and always glycerol as main by-product through a stepwise process (Fig. 3). This phase contains glycerol, unprocessed methanol and a small amount of other substrates and by-products. The mass of crude glycerol is equal to approximately 12 wt% of the obtained mass. The content of pure glycerol in the glycerol phase is about 60–70 wt%, so that besides to the alkaline impurities that need to be removed in the conventional method, glycerol is the main drawback of this method, not only because it suppose a lowering in the atom yield (or atom efficiency) of the process, but also the biodiesel obtained need to be cleaned from the residual glycerol and alkaline impurities through several consecutive washing steps, where it is spent a lot of water, to get the complete glycerol elimination [36–38].

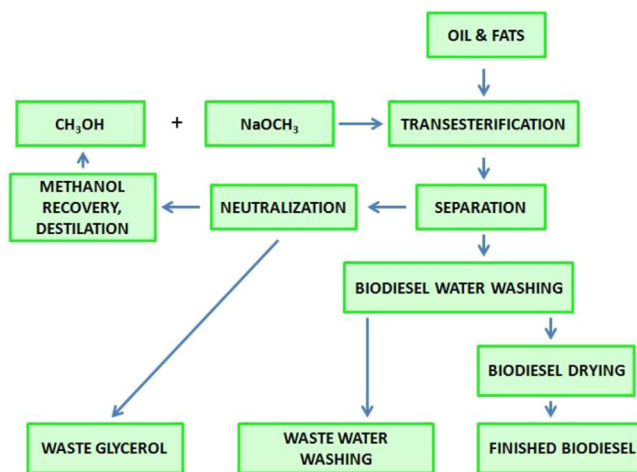


Fig. 4. Biodiesel production process currently used by basic catalysed reactions.

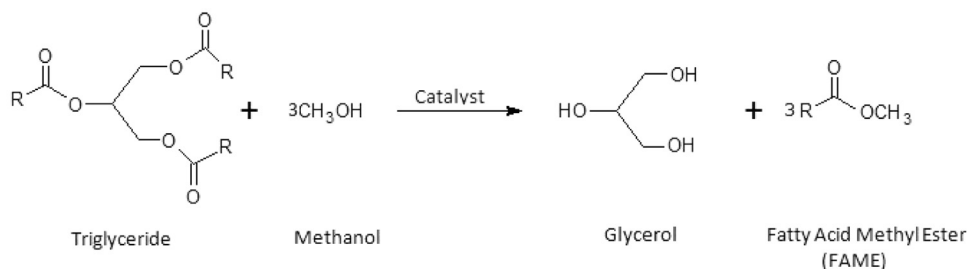


Fig. 3. Outline of the transesterification reaction of triglycerides with methanol (methanolysis) by conventional base catalysis.

A standard design of a biodiesel plant that incorporates a transesterification reaction [12] is shown in the diagram, reflected in Fig. 4. The reaction process is carried out in a reactor under constant agitation at a temperature of 60 °C. Glycerol is then separated by decantation and the excess methanol recovered by distillation. Biodiesel contains catalyst residues which must be neutralized and eliminated before its usage. Biodiesel purification is commonly carried out by neutralization and washing with hot water to remove all impurities. After washing the biodiesel, it is dried in an evaporator to remove residual water that it may contain. Another alternative for the biodiesel purification is the use of resins which absorb impurities. This process consists of a packed column with resin in which is circulated a flow of biodiesel, which leaves the bottom of the column free of contaminants. Depending on the level of contamination of biodiesel and the type of resin, it has a different duration. The resins can go through a washing process to be used again.

Regardless of the procedure to obtain the so-called conventional biodiesel (EN 14214), in all cases the glycerol is collected as a byproduct, representing a notable loss performance of the process, given that the market is already virtually flooded by the glycerine production, precisely obtained as a by-product in the current manufacture of biodiesel [39–41], exacerbated situation in recent years, by the continuous increase in the biodiesel production. Thus, this current method supposes a decreased yield of the process, always higher than nominal 12 wt%, due to the glycerol obtaining as a reaction product, which in very small amount is also incorporated to the biodiesel (FAME) phase. In this respect, the cleaning of glycerol is necessary, because of its reaction ability with oxygen inside the engine at high temperature, where could produce dehydration towards acrolein, that can be polymerised causing several problems, including coking of fuel (Fig. 5). This coking can also generate deposits of carbonaceous compounds on the injector nozzles, pistons and valves in standard engines, thus reducing its efficiency and even its service life [42–45].

2.2. Technological alternatives currently considered to solve the problem of crude glycerol surplus, attained in the production of biodiesel

However, with independence of the higher production cost associated to the glycerol cleaning, the most important handicap for the replacement of a part of fossil fuel by biodiesel is the extraordinary amount of waste glycerol that could be produced. This could be amount 160,000 t per day worldwide, for the

replacement of only a moderated 10 wt% of the 90 million barrels of oil and liquid fuels currently consumed per day, so that the glycerol excess generated may become an environmental problem, since it cannot be disposed of in the environment [46]. This will result in a further decrease of profitability of the biodiesel production unless new glycerol utilizations are found. In fact, the overabundance of glycerol is actually reducing the development of the biodiesel industrial production. This surplus also indicates that the using glycerol technologies present currently many disadvantages and that their efficiency and profitability are yet too low [47].

The simplest utilization method of crude glycerol is its combustion, which is an advantageous method as it does not require any purification, which would increase the cost of the method. However, this process is not easy from a technological point of view. Besides, the heat of combustion is two times lower than that of fossil fuels but is comparable to the combustion heat of most types of biomass (e.g., wood or straw). The calorific value is lower due to the relatively large amount of water that is obtained. Moreover, water renders the combustion of glycerol very difficult because it leads to the blanketing of the flame at the burners and the formation of large quantities of carbon black. In practice, it is essential to perform co-combustion of glycerol with other liquid fuels using special burners, so that the co-combustion of the glycerol/biomass has not yet been carried out in a large scale [47].

Therefore, much scientific work is in progress over the world to obtain innovative processes to spend such byproduct glycerol generated in biodiesel synthesis. The numerous methods using waste glycerol can be categorized according to the obtained products or to the applied technology [48]. In Table 1 are summarized some products obtained and technological alternatives currently studied, to make profitable the excess glycerol generated in biodiesel production.

In summary, it seems that at least some of the pointed out technologies lead to the manufacturing of traditional products that are currently obtained by other technologies, but actually those technologies based on the use of glycerol as raw material, result in a lower profitability in the production of such conventional products. Thus, it is still very difficult to realistically consider the conversion of crude glycerol into useful products, able to offsetting the overrun cost of cleaning the biodiesel, obtained by the conventional transesterification procedure [68–70].

However, to ensure a confident process of replacement of fossil fuels by biofuels is necessary to ensure not only enough oil feedstock and an efficient method for biofuel production but also is mandatory the profitable utilization of all of the by-products and wastes (oilseed cake and crude glycerol) that are generated during the production process. In summary, the process needs to be cost effective at all the three stages of the procedure, not only in the obtaining of the best raw materials by farming the seed most suitable and the obtaining of the corresponding vegetable, edible and/or edible, oils (i.e., rapeseed, soybean sunflower oil or jatropha) and in the transesterification process, as usually it is considered in most publications, but also in the proper management (economic and environmental) of wastes and by-products. With independence of the debate relative to the use of edible oils to produce biodiesel in the long-term due to the increasingly big gap between demand and supply of such oils in many countries (what could limit its expansion capacity), the two former points are at present properly solved, but this is not at all the question of crude glycerol generated in the conventional transesterification process.

In this respect, the large amounts of glycerol obtained have resulted in a dramatic drop of the glycerol price on the market, which means that the traditional products obtained from glycerol has met with the barrier of limited demand. Thus, there are only a limited number of patent and scientific publications on the new

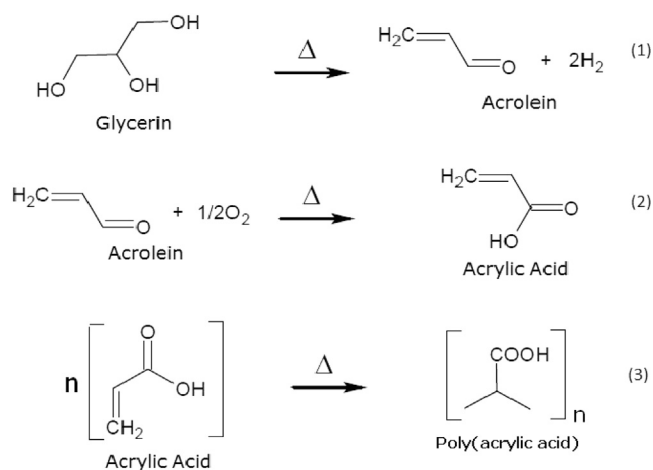


Fig. 5. Processes of dehydration (1), oxidation (2) and polymerization (3) that are developed at higher temperatures inside the engines by the residual glycerol in the biodiesel.

Table 1

Products obtained and technological alternatives currently studied, to make profitable the excess glycerol generated in biodiesel synthesis.

Product	Technology	Ref.
Acrolein	Selective catalytic oxidation on WO ₃ /ZrO ₂ catalysts	[49]
1,2-Propanediol	Hydrogenolysis on Co/MgO	[50]
1,3-Dichloro-2-propanol	Glycerol chlorination in acetic acid as catalyst	[51]
Epichlorohydrin	Glycerol chlorination by gaseous hydrochloric acid	[52]
Di- <i>tert</i> -butyl ethers	Heterogeneous catalytic etherification with <i>tert</i> -butyl alcohol with silica supported acid catalysts	[53]
Monolaurin and dilaurin (mono and diacylglycerols)	Esterification with lauric acid in supercritical CO ₂ (SCC) medium with aluminium and zirconium mesoporous materials	[54]
1,2-Propanediol	Vapor-phase dehydration- hydrogenation on copper metal catalysts at ambient hydrogen pressure.	[55]
Glyceric acid	Selective oxidation in a base-free aqueous solution over different sized Pt catalysts	[56]
Glyceric and tartronic acids	oxidation in the presence of O ₂ and a gold based catalyst	[57,58]
Synthesis gas (H ₂ +CO)	Pyrolysis over carbonaceous catalysts	[59]
Hydrogen	Steam reforming reforming, autothermal reforming, aqueous-phase reforming, supercritical water reforming and photocatalytic reforming	[60–63]
Methane	Anaerobic digestion	[64]
Additional value-added products	Glycerol as a supplementary carbon source for fermentation processes by <i>Blakeslea trispora</i> , <i>Pichia pastoris</i> or fungus <i>Pythium irregulare</i>	[65–67]

conversion methods of glycerol into useful and profitable products and the investigations of innovative technologies are in most cases in the preliminary phase of research. Thus, the production of biodiesel is being In fact slowed because it is needed new advanced methods of using glycerol that are not only industrially feasible but also profitable. These methods should allow the production of higher amounts of chemical products derived from glycerol [47].

3. Petrodiesel-like biofuels obtained by hydro processing of oils and fats in the current oil refining plants: Green diesel

Given the above disadvantages presented by biodiesel, several alternative procedures are currently under development for the conversion of fats and oils into quality biofuels for application in diesel engines. Thus, a number of processes (cracking or pyrolysis, hydrodeoxygenation or hydrocracking) can be used to obtain similar fuels to petrodiesel. In this respect, the catalytic hydrotreating of vegetable oils, in existing refinery processing installations, is one of the best possible solutions [71]. This biofuel has been gaining attention in recent years and can be termed “Green diesel”, a renewable diesel whose composition resembles that of petroleum-derived diesel fuel. Accordingly, feedstocks derived from renewable material can be converted in hydrocarbons, similar to those present in fossil fuels and avoiding the presence of glycerol, by a procedure that is termed hydrocracking. In fact, production of hydrocarbon fuels from vegetable oils by a process that at that time already was termed “cracking”, actually precedes to the first citation of the biodiesel expression. This cracking procedure generally yielded a variety of products including gasoline and petrodiesel-like fuels, where the decomposition of oils was undertaken at high temperatures in the presence of hydrogen so that several papers are concerned with the cracking and hydrocracking terms [71]. The pioneer works on cracking of various vegetable oils were performed in China in the 1930s, where such fuels were used as emergency replacements for petroleum-derived fuels during World War II [72].

Since then, many different catalysts and processes have described to transform various vegetable oils into normal alkanes, in the gasoline or diesel boiling range, by employing a hydrotreating process, mainly in the last decade, when growing concern regarding energy

resources and the environment has increased interest in the study of alternative sources of energy to provide a suitable diesel oil substitute for internal combustion engines [73–91].

Other related technology to transform the triglycerides obtained from renewable sources to produce high quality diesel fuel consists in carry out the hydrotreating of vegetable oils in conventional oil refineries, together with the relevant portions of heavy crude oil of equivalent molecular weights [93–103]. Thus, during quality improvement of mixtures of rapeseed oil and straight run gas oil (sulphur content: 0.95%) on NiMo, P/Al₂O₃ catalyst at different process parameters, it was found that both the deep sulphur and nitrogen removal of gas oil and oxygen removal reactions of triglycerides (hydrogenation, decarboxylation and decarbonylation ways) and in a moderate degree the hydrogenation of aromatics took place. At favourable process parameters (350–360 °C; 60 bar; LHSV: 1.5 h⁻¹; H₂/hydrocarbon ratio: 600 N m³/m³) diesel fuel fractions with sulphur and nitrogen content ≤ 10 mg/kg and with significantly higher cetane numbers (> 60–80) than the requirement of the valid standard (minimum 51; EN 590:2009) were produced. During its application the concentration of sulphur and nitrogen oxides and the particulate matter is clearly lower in the exhaust gas contributing to lower emission and the conversion of the catalytic activity of the after-treatment systems [103].

In this way, renewable liquid alkanes can be produced by treatment of mixtures of vegetable oils and fractions of heavy oil vacuum (HVO), in flows of hydrogen and conventional catalysts currently used in hydrocracking units using conventional catalyst, like sulphured NiMo/Al₂O₃, and many others under usual conditions of pressure and temperatures in the range 300–450 °C. The reaction produced involves hydrogenolysis of C–C bonds of vegetable oils, which leads to a mixture of lower molecular weight alkanes by three different routes: decarbonylation, decarboxylation and hydrodesoxygenation promoted by presulfided commercial hydrotreating NiMo-type catalyst [79], that can be operated in a pilot-plant with hydroprocessing fixed-bed reactor (scheme in Fig. 6), under conditions of 330–390 °C, 3 MPa and 2 h⁻¹ space velocity. Gas by-products are usually H₂, CO, CO₂, O₂, N₂, H₂S, CH₄ and C₂–C₆ hydrocarbons and a significantly high yield range of about 80 wt% of liquid hydrocarbon products are achieved. Moreover, the liquid hydrocarbon products obtained have low acid number, suitable density and viscosity, and quite high cetane index. In this respect, traditional hydrodesulfurization catalysts such as sulfided NiMo/Al₂O₃, CoMo/Al₂O₃, and NiW/Al₂O₃

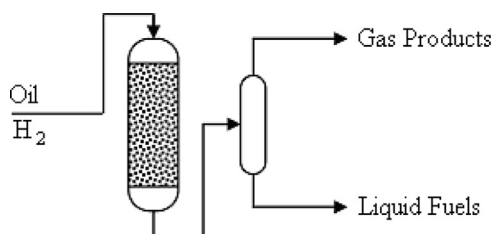


Fig. 6. Production of high quality biodiesel from vegetable oils by hydrotreating together with petroleum hydrocarbons in a fixed-bed reactor, by using a pre-sulfided commercial hydrotreating NiMo-type catalyst, operated at 350 °C. Gas by-products, about 20 wt%, are H₂, CO, CO₂, O₂, N₂H₂S, CH₄ and C₂–C₆ hydrocarbons.

are currently being investigated to obtain renewable diesel in the facilities of conventional oil refineries.

One mechanism involves a simple hydrogenation or hydro-deoxygenation (HDO) reaction, which is described via an adsorbed enol intermediate, and produces water, propane and three normal alkanes of the corresponding length of the fatty acid chains of the oil. By this reaction, one mole of triglyceride reacts with 16 mol of hydrogen (assuming a four double bonds/mole) and forms six moles of water, one mole propane and three moles of a mixture of *n*-C₁₈ and *n*-C₂₂. In the other proposed mechanism, usually called decarboxylation or CO₂-elimination, the triglyceride is broken down into propane, carbon dioxide and/or carbon monoxide and into an *n*-alkane one C-atom shorter than the total length of the fatty acid. For rapeseed oil, the products of the *n*-alkane are *n*-C₁₇ and *n*-C₂₁ [92].

In summary, fossil oil hydrotreating units in refineries were initially aimed to reducing the sulphur content of fuels to accomplish standard specifications in the different countries. However, this process is currently one of the best available technologies to produce biofuels in conventional oil refineries, where the treatment of vegetal oils or animal fats with hydrogen at variable pressures, in the presence of a supported metal catalyst, is able to produce high quality diesel fuels, which are often referred to as renewable diesel, Green diesel or Green oil [102–109].

In this respect, this methodology is specially adapted to be use with oils (non-edible) with higher fatty acid content, because they lead to the formation of soaps, consequent loss of oil and problems of product separation during conventional homogeneous catalytic transesterification with NaOH or KOH. Besides, another advantage of biofuels obtained from hydrotreating vegetable oils respect to the use of biodiesel (methyl and other esters of fatty acids) is related to the fact that in the former case the same components as those present in fossil diesel are obtained, so that filter plugging and cold flow properties are minimized respect to conventional biodiesel. However, there is a decrease in the atom yield of the process (atom efficiency) because there is a significant loss of raw material since the oxygen present in the triglyceride is removed as CO₂ and H₂O [92]. In practice, it is obtained a complete loss of glycerine (like in biodiesel production), but in this way are avoided the biofuel cleaning operations, although it has also less lubricity that biodiesel.

Furthermore, the advantages of hydrotreating over conventional biodiesel obtained by transesterification with methanol are lower processing cost, compatibility with infrastructure, NO_x emission reduction and feedstock flexibility. Thus, the use of HVO enables appreciable reductions in NO_x, PM, HC and CO emissions without any changes to the engine or its control in heavy-duty engines. HVO could play an important role in providing a sustainable source of transportation fuels during the coming decades [110]. Whether it will offer favourable economics or not versus future petroleum-derived fuels or other advanced bio-fuels is not clear at this time; however, a study of the value chain of

biofuels has highlighted several factors that will have major impact on economies of scale and ultimate economics [111]. These factors include the processing capabilities of existing refineries and the advantages from using existing logistic capabilities, especially for the first commercial productions. The capacity to finance timely process development and the corresponding commercial upgrade with its associated risks need also to be considered. In fact, most of the required facilities could be able to operate at comparable scale to that used in the current petroleum-based fuels industry, with substantial cost savings.

In summary, the application of the method of co-processing of oils and fats of any quality, along with fossil diesel in hydrocracking facilities, has notable advantages over the conventional biodiesel production methods, since have not yet been feasible any procedures developed to exploit the residual glycerol, produced in the transesterification process.

4. Biodiesel-like biofuels produced by obtaining various glycerol derivatives in the same transesterification process of oils and fats

To avoid the associated problems with the generation of glycerol in the conventional process, a series of alternative methods are considered to get the highest atom efficiency also avoiding the presence of glycerine. In this respect, the transformation of waste glycerol into oxygen-containing branched compounds it is being currently considered as an interesting solution to provide an outlet for increasing glycerol stocks [46,112]. Thus, several oxygenated compounds, obtained by transformation of glycerol via etherification, esterification and acetalisation, have been assessed as additives or additional components for biodiesel formulation. The addition of these compounds has not only improved the low-temperature properties of biodiesel (i.e., pour point and cold filter plugging point) and viscosity, but also did not impair other important biodiesel quality parameters analyzed. Although most of the studied oxygenated derivatives do not significantly improve any biodiesel quality, they do not exert any significant negative effect.

Together with this strategy, consisting in obtaining adequate oxygenated derivatives after its separation from the transesterification reaction where the glycerol is obtained, another target of great interest currently is the production, in only one reaction, of new biofuels that integrate the glycerol as a derivative product, miscible with the fatty acid methyl or ethyl esters (FAME or FAEE) obtained in a unique transesterification process. Basically, this is possible by using some alternative esters, instead of the alcohol usually employed in the conventional process. Thus, if some glycerol derivative compound is obtained at the same time that FAME (or FAEE) in an interesterification process, a new biofuel is obtained in only one reaction avoiding the presence of glycerol. Thus, this methodology avoids the separation of glycerol before its transformation, simplifying the process and, in a similar way as previously obtained with derivatives of glycerol [46,112], these biofuels not only prevent the generation of waste, but also increase the yields of the process, always higher than nominal 12 wt%, by incorporating some derivatives of glycerol into the reaction products as well as all the reactants used. In this way, the highest atom efficiency, practically 100 wt%, is obtained. Novel methodologies to prepare esters from lipids using different acyl acceptors which directly afford alternative co-products are currently under development [113–115].

The interesterification processes can be performed with the same catalysts applied in transesterification processes (homogeneous or heterogeneous, acid or basic catalysts, lipases, supercritical conditions, etc.), although at present most of these processes, when applied to the biofuels production, are carried out

using different lipases [113], where instead of using methanol, the lipase-catalyzed synthesis of fatty acid alkyl esters can also be performed using alternative alcohol donors such as methyl or ethyl (alkyl) acetate and dimethyl or diethyl carbonate. These mixtures including glycerol derivative molecules have relevant physical properties to be employed as novel biofuels. The atom efficiency is also improved as the total number of atoms involved in the reaction is part of the final mixture. Even the reactants used remain together to the obtained reaction products to be directly used as biofuels.

4.1. Biodiesel-like biofuels produced by obtaining glycerol triacetate in the same transesterification process of oils and fats

Mixtures of fatty acids methyl esters (FAMES) and glycerol triacetate (triacetin) are products of the interesterification reaction of triglycerides with methyl acetate in the presence of strong acid catalysts, so that all these products could be used as components of new type of a patented novel biofuel, which strongly improves economy of the biofuel production according to Fig. 7. Such mixture named Gliperol it is claimed that exhibits fuel characteristic comparable with traditional biodiesel fuel [116–118]. This is composed of a mixture of three molecules of FAMES and one molecule of triacetin and it can be obtained after the interesterification of one mol of TG with three moles of methyl acetate, using an acidic catalyst, molar ratio oil/methyl acetate in the range 1:3 to 1:9, and temperatures in the range 40–200 °C.

However, most studies apply lipases as catalysts in solvent free systems [119–128] or in ionic liquids [129], supercritical conditions [130–135], ultrasound assisted interesterification [136] or KOH homogeneous catalysts are also studied [137–140]. In this respect, the possibility of obtaining Gliperol under most conventional basic conditions has been evaluated obtaining the kinetic parameters for the chemical interesterification of sunflower oil with methyl acetate, with potassium hydroxide, potassium methoxide and polyethylene glycolate as catalysts [137–139]. The chemical interesterification experiments were performed at 30–50 °C and with catalyst-to-oil molar ratios of 0.1:1, 0.15:1 and 0.2:1, respectively. Results obtained indicated the presence of diacetin and monoacetin, together to the triacetin. Under these conditions, when potassium methoxide was used as catalyst, equilibrium was reached within the first 15 min of the reaction. The mass fractions of fatty acid methyl esters (FAME) and triacetin in the product were 76.7% and 17.2%, respectively. Despite the greener character of ethyl acetate, this acyl acceptor is less studied than methyl acetate [113,141–143], although results described indicate similar behaviour that methyl acetate in the interesterification with lipases. However, in this case the corresponding FAEE (instead of FAME) with triacetin are obtained.

Respect to the influence of triacetin on engine performance, there is a high number of studies because this molecule is considered a good solution for the upgrading of residual glycerol

obtained in the conventional synthesis of biodiesel [40,112,144–150]. It is obtained that Triacetin is an anti-knocking additive when it is used along with the biodiesel in DI- diesel engine. The usage of Triacetin as additive reduces also the knocking engine, improving the performance and reduces tail pipe emissions. Among all the fuels blend studied, the combination 10 wt% Triacetin with biodiesel shows encouraging results [151–153]. In this respect, it can be concluded that the interesterification of triglycerides with methyl or ethyl acetate may be an adequate methodology to obtain conventional biodiesel (FAME or FAEE) including also some amount of a well recognized additive like is triacetin.

4.2. Biodiesel-like biofuels produced by obtaining fatty acid glycerol carbonate esters in the same transesterification process of oils and fats

To this purpose, dimethyl carbonate (DMC) can be used as a transesterification reagent for making esters from lipids which directly achieve alternative co-products soluble in the biodiesel solutions. The reaction is rather attractive, as DMC is reputed to be the prototype of green reagents for its health and environmental inertness. In this respect, it deserves to be remarked that raw materials for DMC production, i.e., methanol and carbon monoxide, are derived from syngas which can be produced from the thermochemical conversion of biomass [154]. Therefore, a fuel produced using DMC and vegetable oils or animal fats as raw materials must be considered as an alternative fuel fully derived from renewable resources. Thus, dimethyl carbonate operates as an alternative acyl acceptor, which is neutral, cheap, and non-toxic. The process of such a biodiesel synthesis is irreversible because the intermediate compound (carbonic acid monoacyl ester) immediately decomposes to carbon dioxide and an alcohol [113].

The reaction between triglycerides and DMC produces a mixture of FAMES and cyclic fatty acid glycerol carbonate esters FAGCs, which constitutes a novel biodiesel-like material, named DMC-BioD [155] in the corresponding patent [156]. The interesterification reaction of triglycerides with dimethyl carbonate (DMC), can generate a mixture of FAMES, FAGCs molecules and also glycerol carbonate (GC) as it is indicated in Fig. 8. As catalysts are in fact used several basic catalysts like KOH, sodium methoxide, sodium hydride and some amines [155–160]. The short name glycerol carbonate is currently used for 4-hydroxymethyl-2-oxo-1,3-dioxolan, and glycerol dicarbonate for 4-(methoxycarbonyloxymethyl)-1,3-dioxolan-2-one, that also it is obtained in the interesterification process. These mixtures including glycerol derivative molecules have relevant physical properties to be employed as a new patented biofuel [154] where the atom efficiency is also improved as the total number of atoms involved in the reaction is part of the final mixture.

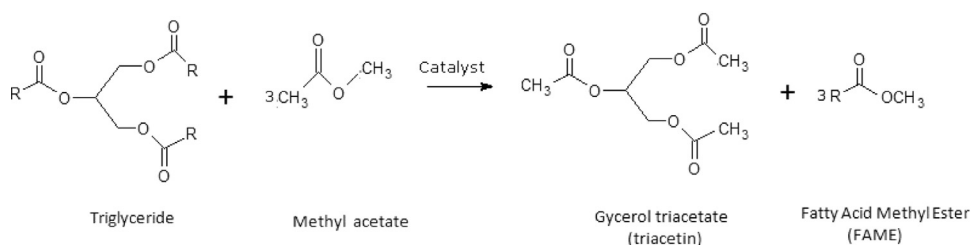


Fig. 7. Gliperol[®] is a novel biofuel proprietary by the Research Institute of Industrial Chemistry Varsow (Poland) [116], formed by a mixture of three moles of FAME and one mole of triacetin, and obtained by interesterification of triglycerides with methyl acetate under strong acidic conditions.

Many efforts have been made in recent years to improve this process where DMC is used as transesterification reagent operating with different catalysts [155–160], supercritical conditions [161–165] or lipases [166–174], because of the reaction is rather attractive, as DMC is reputed to be a prototype of green reagents for its health and environmental inertness [154] and avoided the co-production of glycerol. The main difference between DMC-BioD and biodiesel produced from vegetable oil and methanol (MeOH-biodiesel) is the presence of fatty acid glycerol carbonate monoesters (FAGCs) in addition to FAMES. In this respect, details regarding composition of DMC-BioD as well as physical and reological properties relevant for its use as a fuel have been also studied in some extension [175]. In this respect, the presence of FAGCs promotes some influences both in the behaviour as fuel and in the flow properties, while the distribution of main pyrogenic compounds, including polycyclic aromatic hydrocarbons (PAHs), is little affected.

In summary, respect to benefits and drawbacks of DMC as an alternative reagent for carry out interesterification of oil and fats to produce biofuel from renewable resources and alternative co-products (glycerol carbonate and glycerol dicarbonate), it should be mentioned that DMC is a less toxic chemical than MeOH, that can be currently manufactured by environmentally safe industrial methods, from CO₂ and renewable resources. Moreover, very important triglyceride conversions are obtained by using very different basic catalysts, lipases, supercritical conditions etc., operating under relatively mild conditions. Besides, glycerol carbonate and its derivatives are characterised by low toxicity and the remaining non reacted DMC not need to be separated from the reaction products, because it is an effective additive for diesel engines, due to its high oxygen content [176]. Here we have that the fabrication process is very simplified respect to the conventional biodiesel obtained from methanol.

In this respect, while in the methanolysis process all the glycerol is left as co-product, in the DMC reaction a large fraction of glycerol (may be > 65%) is incorporated into the biofuel in the form of FAGCs and only a minor fraction is converted into glycerol carbonate and dicarbonate [154]. Thus, this option is more profitable than the two steps method where the byproduct glycerol obtained in the conventional transesterification process is transformed, in a second step in glycerol carbonate and dicarbonate [177–180]. These latter compounds obtained in this way may find

better utilisation as additive or chemical intermediates and their introduction into the market may contribute to mitigate the problem of glycerol overproduction due to increasing conventional biodiesel utilisation.

Finally, it can be concluded that the presence of FAGCs in the DMC-BioD reaction mixture has some detrimental effects on flow properties (viscosity values) with respect to the conventional biodiesel (pure FAME); so that its use as pure B100 in present ID engines is not advisable. However, the use of DMC-BioD as an additive for fossil diesel (e.g., at the typical B20, 20/80 biodiesel/diesel ratio) appears to be very adequate for existing diesel engines. The results gathered from pyrolysis experiments support the view that biodiesel is intrinsically less prone to emit PAHs than petroleum diesel. The presence of more oxygenated components (i.e., FAGCs) in DMC-BioD does not affect substantially the emission levels of PAHs and the pattern of hydrocarbons generated upon pyrolysis relative to conventional MeOH-biodiesel.

4.3. Biodiesel-like biofuels produced by obtaining monoacylglycerol in the same transesterification process of oils and fats

In this respect, it was recently developed a protocol for the preparation of a new kind of biodiesel that integrates glycerol into their composition via 1,3-regiospecific enzymatic transesterification of sunflower oil using free [181–183] and immobilized [184–186] pig pancreatic lipase (PPL). Besides, it was found that operating conditions, compared to the conventional biodiesel preparation method, were much smoother and without generation of impurities (acidic or alkaline) under the conditions of reaction process. Thus, the already patented Ecodiesel-100 [181–186] obtained through the 1,3-selective partial ethanolysis of the triglycerides with PPL, is a mixture of two parts of FAEE and one part of MG, that integrates the glycerine as a soluble derivative product (MG) in the diesel fuel, but unlike these methods, no specific reagent (such as dimethyl carbonate or methyl acetate) more expensive than ethanol is used. The procedure takes advantage of the 1,3 selective nature of lipases, which allows to “stop” the process in the second step of the alcoholysis, thereby obtaining a mixture of two moles of FAEE and one of MG, as products Fig. 9. This strategy is based on obtaining an incomplete alcoholysis by application of 1,3-selective lipases, so that the glycerol remains in

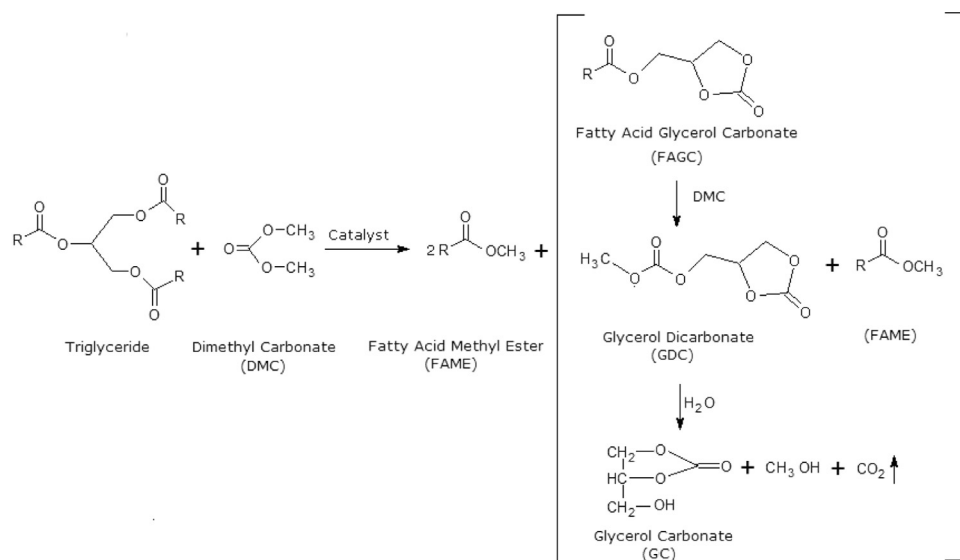


Fig. 8. DMC-BioD[®] is a new biodiesel-like biofuel proprietary by Polimeri Europa (Italy) [156], obtained by reacting oils with dimethyl carbonate (DMC) under alkaline conditions, which avoids the co-production of glycerol by obtaining a mixture of two moles of FAME and one mole of Fatty Acid Glycerol Carbonate (FAGC). This latter can be decomposed generating in this way Glycerol dicarbonate (GDC) and glycerol carbonate (GC) in a variable extension.

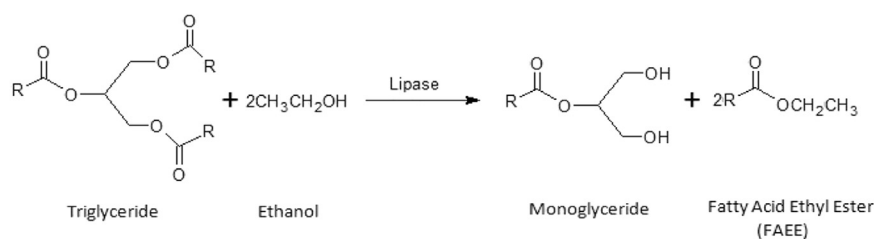


Fig. 9. Ecodiesel-100[®] is a biofuel obtained by enzymatic technology patented by University of Cordoba (UCO) incorporating glycerin, as it is formed of two moles of ethyl esters of fatty acids (FAEE) and one mole of monoglyceride (MG).

the form of monoglyceride which avoids the production of glycerol as by-product, reducing the environmental impact of the process.

In this respect, compared to the conventional method, operating conditions are much smoother, no impurities need to be removed from the final mixture and the biofuel obtained exhibits similar physicochemical properties to those of conventional biodiesel. Last, but not least, monoacylglycerides (MG) was proven to enhance lubricity of biodiesel as it was demonstrated by recent studies [187–189]. Besides, ethanol not spent in the enzymatic process remain in the reaction mixture in such a way that after the reaction the products blend obtained can be directly used as a fuel. In this respect, some studies [190–192] have proven that blends of diesel fuel and ethanol with biodiesel produced some less maximum power output than regular diesel. Besides, no significant difference in the emissions of CO₂, CO, and NO_x between regular diesel and biodiesel, ethanol and diesel blends was observed. But the use of these blends resulted in a reduction of particulate matter. Consequently, such blends can be used in a diesel engine without any modification, taking into account the limited changes obtained respect to the use of pure diesel. Thus, the Ecodiesel expression is currently ascribed to whichever blend of fatty acid alkyl ester with ethanol, alone or with any proportion of diesel fuel [190–193].

On the other hand, the use of conventional biodiesel as a diesel fuel extender and lubricity improver is rapidly increasing. While most of the properties of biodiesel are comparable to petroleum based diesel fuel, improvement of its low temperature flow characteristic still remains one of the major challenges when using biodiesel as an alternative fuel for diesel engines. However, a considerable reduction in pour point has been noticed by using ethanol as cold flow improver [194]. Thus, the performance and emission with ethanol blended biodiesel fuel and ethanol–diesel blended biodiesel fuel have developed a considerable reduction in emission. Ethanol blended biodiesel is totally a renewable, viable alternative fuel for improved cold flow behaviour and better emission characteristics without affecting the engine performance, so that blending bioethanol with diesel fuels is an alternative to incorporate a renewable fraction in vehicle fuels is receiving growing attention for its economic and environmental advantages [195]. In this respect, the Ecodiesel will display some higher cloud points and pour points than conventional biodiesel; however the presence of ethanol as a surplus of the ethanolysis reaction will compensate the low temperature flow characteristics. Besides, several additives may be used to keep the basic chemical functions to improving ignition and combustion efficiency and stabilizing such fuel mixtures [196].

However, an important disadvantage of the conventional biodiesel is its performance in cold weather, which may compromise its year-round commercial viability in moderate temperature climates. Thus, there is evidence that soybean oil fatty acid methyl esters develop operability issues at ambient temperatures about 0 °C. In contrast, petrodiesel develops similar problems at a significantly lower temperature range, typically between –16 and –20 °C. On the other hand, a significant obstacle to the

commercial acceptance of conventional biodiesel is the potential for filter plugging due to precipitates in the fuel. The majority of these precipitates can be attributed to either steryl glucosides (SGs) or monoacylglycerols in biodiesel [197–199]. Thus, monoacylglycerols (MG) play an important influence on the Cold Flow Properties of Biodiesel, through the effects on cloud point (CP), freezing point (FP), cold filter plugging point (CFPP), and wax appearance point (WAP). These parameters are mainly affected by saturated MG that also have low solubility in biodiesel and may form solid residues during storage in cold weather, so that pure monoolein may be problematic with respect to melting transitions between 25 and 33 °C, however solubility data for FAME–MG mixtures exhibits a broad transition temperature range from solid at low temperature to liquid at temperatures exceeding 60 °C. Thus, high amounts of MG increased CP, FP and CFPP [197]. Besides, the formation of precipitate during cold temperature storage was dependent not only on blend concentration but also on the feedstock. Thus, in biodiesel obtained from Soybean oil steryl glucosides are the major cause of precipitate formation while for poultry fat-based biodiesel, the precipitates are due to monoglycerides. However, the precipitates from cottonseed oil-based biodiesel are due to both steryl glucosides and monoglycerides [198].

In this respect, it is under research a cold soak filterability performance test, which will help to identify fuels that may have a propensity to clog filters if exposed to long-term storage in cold weather [200]. Besides, recent studies have proven that biodiesel samples with poor cold flow properties were improved by mixing with biodiesel samples exhibiting better cold flow properties, for practical usage at climate of maximum 0 + °C ± 1 + °C. However, the removal of minor components such as steryl glucosides and monoglycerides did not improve the CFPP [201]. Accordingly, Ecodiesel could have some more limitations than conventional biodiesel when operating under low temperatures, but this handicap could be solved using suitable mixes of biodiesel–petrodiesel–ethanol. In this respect, this methodology should be specifically designed taking into account the oil used as raw material as well as the climate conditions where the biofuel will be used.

5. Conclusions and future prospects

With the declining availability of petroleum resources, deterioration of the world environment, and the increased demand for fuels by emerging economies, it is imperative to develop new routes to produce green renewable fuels to substitute conventional fossil-derived ones.

The use of fossil fuels is unsustainable at medium term due to depleting resources as well as to the accumulation of greenhouse gas emissions, due to the fast consumption of fossil energy, so that it has become increasingly important to develop abatement techniques and adopt policies to promote those renewable energy sources which are capable to minimize the dependency on fossil

reserves and also to maintain environmental and economic sustainability.

Biofuels are an attractive alternative to current petroleum based fuels as they allows the substitution of fossil diesel, without engine modifications, showing also a favourable profile of combustion emissions, producing much less carbon monoxide, sulphur dioxide and unburned hydrocarbons than petroleum-based diesel fuel. Thus, biofuels could play an essential part in reaching targets to replace petroleum based transportation fuels because of they can be direct and immediate replacements for the liquid fuels used in transport that can be easily integrated to the logistic systems that are operating today.

It is a true that in the present energy scenario, a complete substitution of petroleum fuels by biofuels is impossible from the production capacity and from the economical capacity point of views, considering the current gap between prices, but energy security and climate change are the two major driving forces for worldwide biofuel development which also will have the potential to stimulate the agro-industry. Thus, it is an urgent priority the introduction of fuels based upon renewable feedstocks. This process would start as soon as possible and ought to be smooth and gradual, providing the production of the same commodities currently demanded in transport but considering their renewable character and avoiding abrupt changes in the market prices that could activate undesired energetic crisis.

However, the technological option for the massive production of replacing biofuel could not be the current conventional biodiesel under EN 14214, due to the important handicaps exhibited in the procedure of cleaning and production, mainly due to the predictable huge amount of waste glycerol produced. In fact, it is assumed that the delay at present experienced in the introduction of biofuels is associated with the difficulty of obtaining biodiesel according to EN 14214, which is contemplated as FAME mixes, with glycerin strict limits. In this respect, not only is not at this time satisfactory solved the problem of glycerol cleaning, but also there are not adequate technologies for the cost-effective transformation of the huger amounts of glycerol obtained.

In this respect, there is not any process presently able to obtain profitable commodities by using this waste glycerol as raw material. Besides, at the present there is no one definitive technology for residual glycerol cleaning in the FAME, economically viable and able to avoid spending large amounts of water, time and energy like in the existing process. It can be consequently

concluded that the replacement of fossil fuels by renewable ones could not be carried out in the next future by the existing biodiesel, instead of it is easier usage, from the engineering point of view, as it does not require extensive engine modification. Thus, the production of biofuels applicable to diesel engines, without generation of glycerol wastes, that it is difficult to manage and that in turn requires its total elimination of biodiesel, due to the problems that generate in modern Diesel engines (the current limit is $< 0.02\%$ depending) is actually a technological objective of the first magnitude.

However, currently there are a number of available alternative methodologies, in different stages of development, capable of producing suitable biofuels for fossil diesel replacement without glycerol generation. In Table 2 is shown a summary sheet of the pros and cons of different existing methodologies for obtaining biofuels free of glycerin. Thus, several advantages over conventional biodiesel are obtained when petrodiesel-like biofuels are produced by the hydro-processing technology, when it is integrated within a current crude-oil refinery setting. Hydrogen required for the reaction is actually readily available, producing a reliable, pure-paraffin product. In addition, all reaction products are compounds that are found in normal refinery products and do not require any special handling, so that the hydrocarbon products can all be easily blended with conventional refinery products in any proportion.

In this respect, taking into account the very mature procedure to obtain diesel-like biofuels by hydro-treating of oils and fats, in conventional hydro-processing facilities in refineries, currently used to reduce sulphur contain in fossil fuels, the policy makers could implement revision of the legal framework to incentive to the multinational petrol companies to launch in their refinery process that incorporates increasing amounts of renewable oil and fats to fulfill the accorded percentages amounts, in those countries compromised by international treaties in the replacement of fossil fuels by renewable feedstocks.

On the other hand, there are some other methodologies, at present under development, which can produce biodiesel-like biofuels that avoids the generation of glycerol or another byproduct, so that exhibiting 100% atom efficiency. Besides, these biofuels exhibit higher lubricating properties than fossil fuels or even conventional biodiesel. The higher oxygen content with respect to petroleum diesel ensures also more complete combustion and a lower content of CO, hydrocarbons, and particulate in

Table 2

Schematic comparison of the main characteristics of the different technologies available to produce renewable liquid fuels, from vegetable oils.

Biofuel type	Biodiesel EN 14214	Petrodiesel-like biofuels	Biodiesel-like biofuels		
Name	Biodiesel	Green diesel	Gliperol [®]	DMC-BioD [®]	Ecodiesel [®]
Reactive Catalyst Products	Methanol or ethanol NaOH or KOH 3 FAME or 3 FAEE	H ₂ Hydrotreating Ni–Mo type Hydrocarbons C7–C18	Methyl acetate Acid, basic or lipases Glycerol triacetate + 3 FAME No waste	Methyl carbonate Basic or lipases Fatty acid glycerol carbonate + 2 FAME No waste	Ethanol Lipases Monoglycerides + 2 FAEE No waste
Byproducts	Glycerol	CO, CO ₂ , O ₂ , N ₂ , H ₂ S, and C1–C6 hydrocarbons			
Separation process	Complex	Simple	Not needed	Not needed	Not needed
Investment facilities	Medium	Low (high, if the hydroprocessing facilities are not available)	Low	Low	Low
Free fatty acids and/or water in the starting oil	Free fatty acids are Transformed to soaps	Free fatty acids are transformed to biofuel	Free fatty acids are transformed to biofuel	Free fatty acids are transformed to biofuel	Free fatty acids are transformed to biofuel
Catalyst cost	Low	Medium	Low (high if lipases)	Low (high if lipases)	High
Environmental impact	High. alkaline and saline effluents are generated. Wastewater treatment is needed	Low	Low	Low	Low

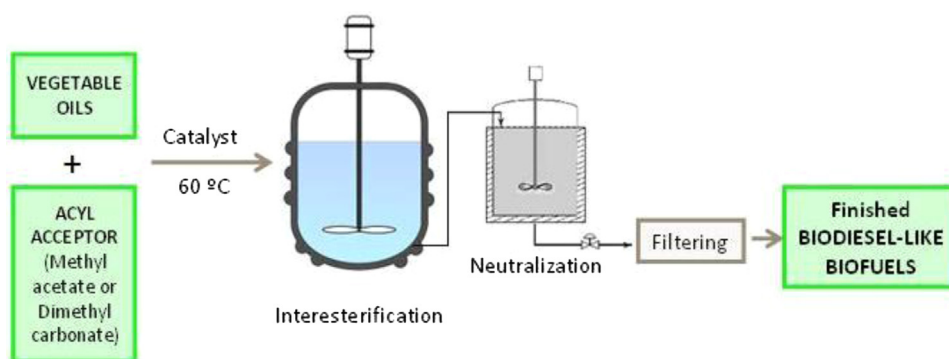


Fig. 10. Production process of Biodiesel-like biofuels by interesterification of vegetable oils with methyl acetate or methyl carbonate, used as acyl acceptors.

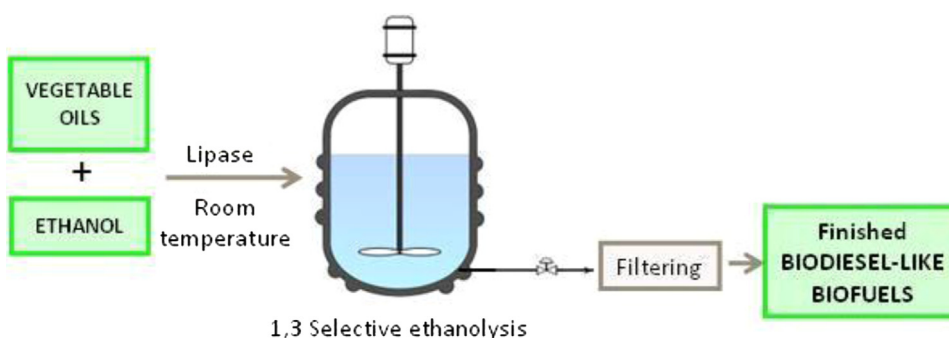


Fig. 11. Production process of Biodiesel-like biofuels by selective ethanolysis of vegetable oils using lipases as biocatalyst.

emissions. At the same time, these technologies that integrates glycerine as derivates (glycerol acetate, fatty acid glycerol carbonate esters or as monoglycerides simply), can also be profitably applied to a very small production scale and with a minimal investment, compared with current oil refineries, so that it could be installed in areas close to where crops are produced (the biofuel plant is become actually in an additional treatment after the oil extraction of crops), so that it become clearly more competitive than the hydrotreating technology for biofuel production in areas of low productivity and geographically dispersed, where logistical problems could be particularly limiting.

In this respect, the simplicity of the production process of Biodiesel-like biofuels by interesterification of vegetable oils with methyl acetate or methyl carbonate, used as acyl acceptors (shown in Fig. 10), as well as those of biofuels obtained by selective ethanolysis of vegetable oils using lipases as biocatalyst, (in Fig. 11) can be compared with biodiesel production process currently used by basic catalyzed reactions, in Fig. 4.

The development and maturation of these new technologies, that produce biofuels applicable to diesel engines in similar way that biodiesel, but without generating unwieldy waste glycerine, avoiding in this way any cleaning process with an additional high cost in water and energy. In this way, it is expected to boost up the use of biofuels, to create a scenery with opportunities for small and medium enterprises for producing biofuels in very diverse geographical areas, where being possible the cultivation of plants suitable for its transformation “in situ” into biofuels. Thus, agriculture can play an increasingly important role through the production of new crops capable of supplying to industrial and energy sectors that now are completely dependent on petroleum.

Similarly, the residues of forest, agricultural, fishing and animal could be upgraded to biofuels, incorporating added value to middle and small enterprises. Thus, different countries, depending on its development possibilities could incentive those procedures more fitted to its circumstances to progress to the continued and

stable replacement of fossil fuels, by more accessible renewable feedstocks.

Consequently, it seems to be a priority the amendment of the legal framework in those countries decided to carry out a gradually and sustained replacement of fossil fuels, with the avowed objective of promoting the use of these new biofuels, to let that they could have the opportunity for accomplish the role initially assigned in exclusive to the conventional biodiesel, according to EN 14214. This new legal scenario will hopefully generate opportunities for the establishments of technology-based companies, in which they perform the maturation of these technologies to obtain at the short/medium term get increasing rates gradually, to get to replace the use of fossil fuels in the long term avoiding in this way the shadow of some unwanted energetic crisis.

Acknowledgements

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References

- [1] Khan SA, Rashmi, Hussain MZ, Prasad S, Banerjee UC. Prospects of biodiesel production from microalgae in India. *Renewable Sustainable Energy Rev* 2009;13:2361–72.
- [2] Chen D, Liu CJ. A current perspective on catalysis for new energy technologies. *ChemCatChem* 2011;3:423–5.
- [3] Li Q, Guo B, Yu J, Ran J, Zhang B, Yan H, Gong J. Highly efficient visible-light-driven photocatalytic hydrogen production of CdS-cluster-decorated graphene nanosheets. *J Am Chem Soc* 2011;133:10878–84.
- [4] Pearson M, Wollersheim C, Hileman J. A techno-economic review of hydroprocessed renewable esters and fatty acids for jet fuel production. *Biofuels, Bioprod Biorefin* 2013;7:89–96.

- [5] Dhar A, Kevin R, Agarwal AK. Production of biodiesel from high-FFA neem oil and its performance, emission and combustion characterization in a single cylinder DICl engine. *Fuel Process Technol* 2012;97:118–29.
- [6] Yusuf NNAN, Kamarudin SK, Yaakub Z. Overview on the current trends in biodiesel production. *Energy Convers Manage* 2011;52:2741–51.
- [7] Borges ME, Díaz L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review. *Renewable Sustainable Energy Rev* 2012;16:2839–49.
- [8] Helwani Z, Othman MR, Aziz N, Fernando WJN, Kim J. Technologies for production of biodiesel focusing on green catalytic techniques: a review. *Fuel Process Technol* 2009;90:1502–14.
- [9] Smith B, Greenwell HC, Whiting A. Catalytic upgrading of tri-glycerides and fatty acids to transport biofuels. *Energy Environ Sci* 2009;2:262–71.
- [10] Juan JC, Kartika DA, Wu TY, Hin TYY. Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: an overview. *Bioresour Technol* 2011;102:452–60.
- [11] Demirbas A. Political, economic and environmental impacts of biofuels: a review. *Appl Energy* 2009;86:108–17.
- [12] Oh PP, Lau HLN, Chen J, Chong MF, Choo YM. A review on conventional technologies and emerging process intensification (PI) methods for biodiesel production. *Renewable Sustainable Energy Rev* 2012;16:5131–45.
- [13] Luque R, Herrero-Davila L, Campelo JM, Clark JH, Hidalgo JM, Luna D, Marinas JM, Romero AA. Biofuels: a technological perspective. *Energy Environ Sci* 2008;1:513–96.
- [14] Verziu M, Coman SM, Richards R, Parvulescu V. Transesterification of vegetable oils over CaO catalysts. *Catal Today* 2011;167:64–70.
- [15] Soriano Jr NU, Venditti R, Argyropoulos DS. Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. *Fuel* 2009;88:560–5.
- [16] Guan G, Kusakabe K, Sakurai N, Moriyama K. Transesterification of vegetable oil to biodiesel fuel using acid catalysts in the presence of dimethyl ether. *Fuel* 2009;88:81–6.
- [17] Aransiola EF, Daramola MO, Ojumu TV, Solomon BO, Layokun SK. Homogeneously catalyzed transesterification of Nigerian *Jatropha curcas* oil into biodiesel: a kinetic study. *Mod Res Catal* 2013;2:83–9.
- [18] Macario A, Verri F, Diaz U, Corma A, Giordano G. Pure silica nanoparticles for liposome/lipase system encapsulation: application in biodiesel production. *Catal Today* 2013;204:148–55.
- [19] Macario A, Giordano G. Catalytic conversion of renewable source for biodiesel production: a comparison between biocatalysts and inorganic catalysts. *Catal Lett* 2013;143:159–68.
- [20] Luque R, Clark JH. Biodiesel-like biofuels from simultaneous transesterification/esterification of waste oils with a biomass-derived solid acid catalyst. *ChemCatChem* 2011;3:594–7.
- [21] Singh Chouhan AP, Sarma AK. Modern heterogeneous catalysts for biodiesel production: a comprehensive review. *Renewable Sustainable Energy Rev* 2011;15:4378–99.
- [22] Viola E, Blasi A, Valerio V, Guidi I, Zimbardi F, Braccio G, Giordano G. Biodiesel from fried vegetable oils via transesterification by heterogeneous catalysis. *Catal Today* 2012;179:185–90.
- [23] Patil P, Deng S, Rhodes JI, Lammers PJ. Conversion of waste cooking oil to biodiesel using ferric sulphate and supercritical methanol processes. *Fuel* 2010;89:360–4.
- [24] Anitescu G, Bruno TJ. Fluid properties needed in supercritical transesterification of triglyceride feedstocks to biodiesel fuels for efficient and clean combustion—a review. *J Supercrit Fluids* 2012;63:133–49.
- [25] Quesada-Medina J, Olivares-Carrillo P. Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol. *J Supercrit Fluids* 2011;56:56–63.
- [26] Demirbas A. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Prog Energy Combust Sci* 2005;31:466–87.
- [27] Chen YH, Huang YH, Lin RH, Shang NC. A continuous-flow biodiesel production process using a rotating packed bed. *Bioresour Technol* 2010;101:668–73.
- [28] Serio MD, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. *Energy Fuels* 2008;22:207–17.
- [29] Vicente G, Martinez M, Aracil J. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresour Technol* 2004;92:297–305.
- [30] Liu X, He H, Wang Y, Zhu S, Piao X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel* 2008;87:216–21.
- [31] Guan G, Kusakabe K, Moriyama K, Sakurai N. Transesterification of sunflower oil with methanol in a microreactor. *Ind Eng Chem Res* 2009;48:1357–63.
- [32] Guan G, Teshima M, Sato C, Son SM, Irfan MF, Kusakabe K, Ikeda N, Lin TJ. Two-phase flow behavior in microtube reactors during biodiesel production from waste cooking oil. *AIChE J* 2010;56:1383–90.
- [33] Behzadi S, Farid MM. Production of biodiesel using a continuous gas–liquid reactor. *Bioresour Technol* 2009;100:683–9.
- [34] Son SM, Kusakabe K. Transesterification of sunflower oil in a countercurrent trickle-bed reactor packed with a CaO catalyst. *Chem Eng Process* 2011;50:650–4.
- [35] Meng YL, Tian SJ, Li SF, Wang BY, Zhang MH. Transesterification of rapeseed oil for biodiesel production in trickle-bed reactors packed with heterogeneous Ca/Al composite oxide-based alkaline catalyst. *Bioresour Technol* 2013;136:730–4.
- [36] Saleh J, Dubé MA, Tremblay AY. Separation of glycerol from FAME using ceramic membranes. *Fuel Process Technol* 2011;82:1305–10.
- [37] Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. The effects of water on biodiesel production and refining technologies: a review. *Renewable Sustainable Energy Rev* 2012;16:3456–70.
- [38] Hasheminejad M, Tabatabaei M, Mansourpanah Y, Khatami far M, Javani A. Upstream and downstream strategies to economize biodiesel production. *Bioresour Technol* 2011;102:461–8.
- [39] Leoneti AB, Aragão-Leoneti V, Oliveira SVWB. Glycerol as a byproduct of biodiesel production in Brazil: alternatives for the use of unrefined glycerol. *Renewable Energy* 2012;45:138–45.
- [40] Rahmat N, Abdullah AZ, Mohamed AR. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: a critical review. *Renewable Sustainable Energy Rev* 2010;14:987–1000.
- [41] Johnson DT, Taconi KA. The glycerin glut: options for the value-added conversion of crude glycerol resulting from biodiesel production. *Environ Prog* 2007;26:338–48.
- [42] Jayed MH, Masjuki HH, Kalam MA, TMI Mahlia, Husnawan M, Liaquat AM. Prospects of dedicated biodiesel engine vehicles in Malaysia and Indonesia. *Renewable Sustainable Energy Rev* 2011;15:220–35.
- [43] Katryniok B, Paul S, Bellière-Baca V, Rey P, Dumeignil F. Glycerol dehydration to acrolein in the context of new uses of glycerol. *Green Chem* 2010;12:2079–98.
- [44] Atadashi IM, Aroua MK, Abdul Aziz A. High quality biodiesel and its diesel engine application: a review. *Renewable Sustainable Energy Rev* 2010;14:1999–2008.
- [45] Jaichandar S, Annamalai K. the status of biodiesel as an alternative fuel for diesel engine—an overview. *J Sustainable Energy Environ* 2011;2:71–5.
- [46] Mota CJA, da Silva CXA, Rosenbach Jr N, Costa J, da Silva F. Glycerin derivatives as fuel additives: the addition of glycerol/acetone ketal (solketal) in gasoline. *Energy Fuels* 2010;24:2733–6.
- [47] Stelmachowski M. Utilization of glycerol, a by-product of the transesterification process of vegetable oils: a review. *Ecol Chem Eng S* 2011;18:9–30.
- [48] Zheng Y, Chen X, Shen Y. Commodity chemicals derived from glycerol, an important biorefinery feedstock. *Chem Rev* 2008;108:5253–77.
- [49] Ulgen A, Hoelderich W. Conversion of glycerol to acrolein in the presence of WO₃/ZrO₂ catalysts. *Catal Lett* 2009;131:122–8.
- [50] Guo X, Li Y, Shi R, Liu Q, Zhan E, Shen W. Co/MgO catalysts for hydrogenolysis of glycerol to 1,2-propanediol. *Appl Catal, A: Gen* 2009;371:108–13.
- [51] Luo Z-H, You X-Z, Li H-R. Direct preparation kinetics of 1,3-dichloro-2-propanol from glycerol using acetic acid catalyst. *Ind Eng Chem Res* 2009;48:446–52.
- [52] Santacesaria E, Tesser R, Di Serio M, Casale L, Verd D. New process for producing epichlorohydrin via glycerol chlorination. *Ind Eng Chem Res* 2010;49:964–70.
- [53] Frusteri F, Arena F, Bonura G, Cannilla C, Spadaro L, Di Blasi O. Catalytic etherification of glycerol by *tert*-butyl alcohol to produce oxygenated additives for diesel fuel. *Appl Catal, A: Gen* 2009;367:77–83.
- [54] Sakthivel A, Nakamura R, Komura K, Sugi Y. Esterification of glycerol by lauric acid over aluminium and zirconium containing mesoporous molecular sieves in supercritical carbon dioxide medium. *J Supercrit Fluids* 2007;42:219–25.
- [55] Akiyama M, Sato S, Takahashi R, Inui K, Yokota M. Dehydration-hydrogenation of glycerol into 1,2-propanediol at ambient hydrogen pressure. *Appl Catal, A: Gen* 2009;371:60–6.
- [56] Liang D, Gao J, Wang J, Chen P, Hou Z, Zheng X. Selective oxidation of glycerol in a base-free aqueous solution over different sized Pt catalysts. *Catal Commun* 2009;10:1586–90.
- [57] Prati L, Spontoni P, Gaiassi A. From renewable to fine chemicals through selective oxidation: the case of glycerol. *Top Catal* 2009;52:288–96.
- [58] Zope BN, Davis RJ. Influence of reactor configuration on the selective oxidation of glycerol over Au/TiO₂. *Top Catal* 2009;52:269–77.
- [59] Fernandez Y, Arenillas A, Diez MA, Pis JJ, Menendez JA. Pyrolysis of glycerol over activated carbons for syngas production. *J Anal Appl Pyrolysis* 2009;84:145–50.
- [60] Adhikari S, Fernando SD, FSD To, Brick MR, Steel PH, Haryanto A. Conversion of glycerol to hydrogen via a steam reforming process over nickel catalysts. *Energy Fuels* 2008;22:1220–6.
- [61] Adhikari S, Fernando S, Haryanto A. Hydrogen production from glycerol: an update. *Energy Convers Manage* 2009;50:2600–4.
- [62] Kunkes EL, Soares RR, Simonetti DA, Dumesic JA. An integrated catalytic approach for the production of hydrogen by glycerol reforming coupled with water–gas shift. *Appl Catal, B: Environ* 2009;90:693–8.
- [63] Gombac V, Sordelli L, Montini T, Delgado JJ, Adamski A, Adami G, Cargnello M, Bernal S, Fornasiero P. CuO_x-TiO₂ photocatalysts for H₂ production from ethanol and glycerol solutions. *J Phys Chem A* 2010;114:3916–25.
- [64] Siles-López JA, Martín-Santos AM, Chica-Pérez AF, Martín-Martín A. Anaerobic digestion of glycerol derived from biodiesel manufacturing. *Bioresour Technol* 2009;100:5609–15.
- [65] Mantzouridou F, Naziri E, Tsimidou MZ. Industrial glycerol as a supplementary carbon source in the production of β -carotene by *Blakeslea trispora*. *J Agric Food Chem* 2008;56:2668–75.
- [66] Celik E, Ozbay N, Oktar N, Cülek P. Use of biodiesel by-product crude glycerol as the carbon source for fermentation processes by recombinant *Pichia pastoris*. *Ind Eng Chem Res* 2008;47:2985–90.

- [67] Athalye SK, Garcia RA, Wen Z. Use of biodiesel-derived crude glycerol for producing eicosapentaenoic acid (EPA) by the fungus *Pythium irregulare*. *J Agric Food Chem* 2009;57:2739–44.
- [68] Hersczki Z, Kazmi A, Clark JH, Luna D. Secondary processing of plant oil (chapter 4). In: Kazmi A, Clark JJ, Kraus GA, editors. *Advanced oil crop biorefineries: RSC green chemistry series no. 14*. London; 2012. p. 166–202.
- [69] Hajek M, Skopal F. Treatment of glycerol phase formed by biodiesel production. *Bioresour Technol* 2010;101:3242–5.
- [70] Suppes GJ. Glycerol technology options for biodiesel industry. In: Knothe G, Krahl J, Van Gerpen J, editors. *The biodiesel handbook*. Urbana: AOCS Press; 2010. p. 439–55.
- [71] Knothe G. Biodiesel and renewable diesel: a comparison. *Progr Energy Combust Sci* 2010;36:364–73.
- [72] Chang CC, Wan SW. China's motor fuels from tung oil. *Ind Eng Chem* 1947;39:1543–8.
- [73] Arvidsson R, Persson S, Fröling M, Svanström M. Life cycle assessment of hydrotreated vegetable oil from rape, oil palm and Jatropha. *J Cleaner Prod* 2011;19:129–37.
- [74] Lapuerta M, Villajos M, Agudelo JM, Boehman AL. Key properties and blending strategies of hydrotreated vegetable oil as biofuel for diesel engines. *Fuel Process Technol* 2011;92:2406–11.
- [75] Veriansyah B, Han JY, Kim SK, Hong SA, Kim YJ, Lim JS, Shu YW, Oh SG, Kim J. Production of renewable diesel by hydroprocessing of soybean oil: effect of catalysts. *Fuel* 2012;94:578–85.
- [76] Sotelo-Boyás R, Liu Y, Minowa T. Renewable diesel production from the hydrotreating of rapeseed oil with Pt/zeolite and NiMo/Al₂O₃ catalysts. *Ind Eng Chem Res* 2011;50:2791–9.
- [77] Liu Y, Sotelo-Boyás R, Murata K, Minowa T, Sakanishi K. Hydrotreatment of vegetable oils to produce bio-hydrogenated diesel and liquefied petroleum gas fuel over catalysts containing sulfided Ni–Mo and solid acids. *Energy Fuels* 2011;25:4675–85.
- [78] Templis Ch Vonortas A, Sebos I, Papayannakos N. Vegetable oil effect on gasoil HDS in their catalytic co-hydroprocessing. *Appl Catal, B: Environ* 2011;104:324–9.
- [79] Shi N, Liu Q, Jiang T, Wang T, Ma LI, Zhang Q, Zhang X. Hydrodeoxygenation of vegetable oils to liquid alkane fuels over Ni/HZSM-5 catalysts: methyl hexadecanoate as the model compound. *Catal Commun* 2012;20:80–4.
- [80] Wang C, Tian Z, Wang L, Xu R, Liu Q, Ma H, Wang BB. One-step hydrotreatment of vegetable oil to produce high quality diesel-range alkanes. *ChemSusChem* 2012;5:1974–83.
- [81] Sivasamy A, Cheah KY, Fornasiero P, Kemausor F, Zinoviev S, Miertus S. Catalytic applications in the production of biodiesel from vegetable oils. *ChemSusChem* 2009;2:278–300.
- [82] Tiwari R, Rana RS, Kumar R, Verma D, Kumar R, Joshi RK, Garg MO, Sinha AK. Hydrotreating and hydrocracking catalysts for processing of waste soya-oil and refinery-oil mixtures. *Catal Commun* 2011;12:559–62.
- [83] Giannakopoulou K, Lukas M, Vasiliev A, Brunner C, Schnitzer H. Low pressure catalytic co-conversion of biogenic waste (rapeseed cake) and vegetable oil. *Bioresour Technol* 2010;101:3209–19.
- [84] Han J, Duan J, Chen P, Lou H, Zheng X, Hong H. Carbon-supported molybdenum carbide catalysts for the conversion of vegetable oils. *ChemSusChem* 2012;5:727–33.
- [85] Serrano-Ruiz JC, Ramos-Fernández EV, Sepúlveda-Escribano A. From biodiesel and bioethanol to liquid hydrocarbon fuels: new hydrotreating and advanced microbial technologies. *Energy Environ Sci* 2012;5:5638–52.
- [86] Gong S, Shinozaki A, Shi M, Qian EW. Hydrotreating of Jatropha oil over alumina based catalysts. *Energy Fuels* 2012;26:2394–9.
- [87] Toba M, Abe Y, Kuramochi H, Osako M, Mochizuki T, Yoshimura Y. Hydrodeoxygenation of waste vegetable oil over sulfide catalysts. *Catal Today* 2011;164:533–7.
- [88] Šimáček P, Kubička D, Kubičková I, Homola F, Pospíšil M, Chudoba J. Premium quality renewable diesel fuel by hydroprocessing of sunflower oil. *Fuel* (<http://www.sciencedirect.com/science/journal/00162361/90/72011>); 90: 2473–2479.
- [89] Bezergianni S, Kalogianni A, Dimitriadis A. Catalyst evaluation for waste cooking oil hydroprocessing. *Fuel* 2012;93:638–41.
- [90] Peng B, Yuan X, Zhao C, Lercher JA. Stabilizing catalytic pathways via redundancy: selective reduction of microalgae oil to alkanes. *J Am Chem Soc* 2012;134:9400–5.
- [91] Liu J, Liu C, Zhou G, Shen S, Rong L. Hydrotreatment of Jatropha oil over NiMoLa/Al₂O₃ catalyst. *Green Chem* 2012;14:2499–505.
- [92] Donniss B, Egeberg RG, Blom P, Knudsen KG. Hydroprocessing of bio-oils and oxygenates to hydrocarbons. understanding the reaction routes. *Top Catal* 20; 52: 229–240.
- [93] Huber GW, O'Connor P, Corma A. Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Appl Catal, A: Gen* 2007;329:120–9.
- [94] Mercader FM, Groeneveld MJ, Kersten SRA, Way NWJ, Schaverien CJ, Hogenboom JA. Production of advanced biofuels: co-processing of upgraded pyrolysis oil in standard refinery units. *Appl Catal, B: Environ* 2010;96:57–66.
- [95] Corma A, Huber GW, Sauvanoud L, O'Connor P. Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. *J Catal* 2007;247:307–27.
- [96] Corma A, Renz M, Schaverien C. Coupling fatty acids by ketonic decarboxylation using solid catalysts for the direct production of diesel, lubricants and chemicals. *ChemSusChem* 2008;1:739–41.
- [97] Lappas AA, Bezergianni S, Vasalos IA. Production of biofuels via co-processing in conventional refining processes. *Catal Today* 2009;145:55–62.
- [98] Melero JA, Clavero MA, Calleja G, García A, Miravalles R, Galindo T. Production of biofuels via the catalytic cracking of mixtures of crude vegetable oils and nonedible animal fats with vacuum gas oil. *Energy Fuels* 2010;24:707–17.
- [99] Fogassy G, Thegarid N, Toussaint G, van Veen AC, Schuurman Y, Mirodatos C. Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. *Appl Catal, B: Environ* 2010;96:476–85.
- [100] Tóth C, Baladincz P, Kovács S, Hancsók J. Producing clean diesel fuel by co-hydrogenation of vegetable oil with gas oil. *Clean Technol Environ Policy* 2011;13:581–5.
- [101] Wan L, Zhang S-P, Li Q-Y, Xu Q-L, Yan Y-J. Co-processing the high-boiling fraction of bio-oil with paraffin oil. *Energy Sources, Part A: Recovery Util Environ Effects* 2013;35:717–24.
- [102] Rana BS, Kumar R, Tiwari R, Kumar R, Joshi RK, Garg MO, Sinha AK. Transportation fuels from co-processing of waste vegetable oil and gas oil mixtures. *Biomass Bioenergy* 2013;56:43–52.
- [103] Hancsók J, Krár M, Kasza T, Kovács S, Tóth C, Varga Z. Investigation of hydrotreating of vegetable oil-gas oil mixtures. *J Environ Sci Eng* 2011;5:500–7.
- [104] Chen S. Green oil production by hydroprocessing. *Intern J Clean Coal Energy* 2012;1:43–55.
- [105] Jha MK, Sinha AK, Agnihotri P. Hydroprocessing of Jatropha oil to produce green fuels. *Int J ChemTech Res* 2013;5:765–70.
- [106] Bezergianni S, Dimitriadis A. Comparison between different types of renewable diesel. *Renewable Sustainable Energy Rev* 2013;21:110–6.
- [107] Satyarthi JK, Chiranjeevi T, Gokak DT, Viswanathan PS. An overview of catalytic conversion of vegetable oils/fats into middle distillates. *Catal Sci Technol* 2013;3:70–80.
- [108] Naika SN, Goudb VV, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. *Renewable Sustainable Energy Rev* 2010;14:578–97.
- [109] Melero JA, Iglesias J, García A. Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges. *Energy Environ Sci* 2012;5:7393–420.
- [110] No SY. Application of hydrotreated vegetable oil from triglyceride based biomass to CI engines—a review. *Fuel* 2014;115:88–96.
- [111] Arbogast S, Bellman D, Paynter JD, Wykowski J. Advanced bio-fuels from pyrolysis oil: the impact of economies of scale and use of existing logistic and processing capabilities. *Fuel Process Technol* 2012;104:121–7.
- [112] Melero JA, Vicente G, Morales G, Paniagua M, Bustamante J. Oxygenated compounds derived from glycerol for biodiesel formulation: influence on EN 14214 quality parameters. *Fuel* 2010;89:2011–8.
- [113] Adamczak M, Bornscheuer UT, Bednarski W. The application of biotechnological methods for the synthesis of biodiesel. *Eur J Lipid Sci Technol* 2009;111:808–13.
- [114] Vasudevan PT, Briggs M. Biodiesel production—current state of the art and challenges. *J Ind Microbiol Biotechnol* 2008;35:421–30.
- [115] Ganesan D, Rajendran A, Thangavelu V. An overview on the recent advances in the transesterification of vegetable oils for biodiesel production using chemical and biocatalysts. *Rev Environ Sci Biotechnol* 2009;8:367–94.
- [116] Kijenski J, Lipkowski A, Walisiewicz-Niedbalska W, Gwardiak H, Rożyczki K, Pawlak I. A biofuel for compression-ignition engines and a method for preparing the biofuel. *European Patent EP1580255*; 2004.
- [117] Kijenski J, Rożyczki K, Lipkowski AW, Walisiewicz-Niedbalska W. New ester biofuel Gliperol (R). *Przemysł Chem* 2007;86:269–72.
- [118] Kijenski J. Biorefineries: from biofuels to the chemicalization of agricultural products. *Polish J Chem Technol* 2007;9:42–5.
- [119] Demirbas A. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Convers Manage* 2008;49:125–30.
- [120] Xu Y, Du W, Liu D, Zeng J. A novel enzymatic route for biodiesel production from renewable oils in a solvent-free medium. *Biotechnol Lett* 2003;25:1573–6.
- [121] Xu Y, Du W, Liu D. Study on the kinetics of enzymatic interesterification of triglycerides for biodiesel production with methyl acetate as the acyl acceptor. *J Mol Catal B: Enzym* 2005;32:241–5.
- [122] Du W, Xu Y, Liu D, Zeng J. Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. *J Mol Catal B: Enzym* 2004;30:125–9.
- [123] Orçaire O, Buisson P, Pierre AC. Application of silica aerogel encapsulated lipases in the synthesis of biodiesel by transesterification reactions. *J Mol Catal B: Enzym* 2006;42:106–13.
- [124] Usai EM, Gualdi E, Solinas V, Battistel E. Simultaneous enzymatic synthesis of FAME and triacetyl glycerol from triglycerides and methyl acetate. *Bioresour Technol* 2010;101:7707–12.
- [125] Huang Y, Yan Y. Lipase-catalyzed biodiesel production with methyl acetate as acyl acceptor. *Z Naturforsch C: Biosci* 2008;63:297–302.
- [126] Ognjanovic N, Bezbradica D, Knezevic-Jugovic Z. Enzymatic conversion of sunflower oil to biodiesel in a solvent-free system: process optimization and the immobilized system stability. *Bioresour Technol* 2009;100:5146–5154.

- [127] Talukder MMR, Das P, Fang TS, Wu JC. Enhanced enzymatic transesterification of palm oil to biodiesel. *Biochem Eng J* 2011;55:119–22.
- [128] Vasudevan PT, Fu B. Environmentally sustainable biofuels: advances in biodiesel research. *Waste Biomass Valorization* 2010;1:47–63.
- [129] Ruzich NI, Bassi AS. Investigation of enzymatic biodiesel production using ionic liquid as a co-solvent. *Can J Chem Eng* 2010;68:277–84.
- [130] Saka S, Isayama Y. A new process for catalyst-free production of biodiesel using supercritical methyl acetate. *Fuel* 2009;88:1307–13.
- [131] Tan KT, Lee KT, Mohamed AR. A glycerol-free process to produce biodiesel by supercritical methyl acetate technology: an optimization study via response surface methodology. *Bioresour Technol* 2010;101:965–9.
- [132] Campanelli P, Banchemo M, Manna L. Synthesis of biodiesel from edible, non-edible and waste cooking oils via supercritical methyl acetate transesterification. *Fuel* 2010;89:3675–82.
- [133] Niza NM, Tan K, Ahmad Z, Lee KT. Comparison and optimisation of biodiesel production from *Jatropha curcas* oil using supercritical methyl acetate and methanol. *Chem Pap* 2011;65:721–9.
- [134] Niza NM, Tan KT, Lee KT, Ahmad Z. Biodiesel production by non-catalytic supercritical methyl acetate: thermal stability study. *Appl Energy* 2013;101:198–202.
- [135] Goembira F, Matsuura K, Saka S. Biodiesel production from rapeseed oil by various supercritical carboxylate esters. *Fuel* 2012;97:373–8.
- [136] Maddikeri GL, Pandit AB, Gogate PR. Ultrasound assisted interesterification of waste cooking oil and methyl acetate for biodiesel and triacetin production. *Fuel Process Technol* 2013;116:241–9.
- [137] Casas A, Ramos MJ, Pérez A. Product separation after chemical interesterification of vegetable oils with methyl acetate. Part II: Liquid–liquid equilibrium. *Ind Eng Chem Res* 2012;51:10201–6.
- [138] Casas A, Ramos MJ, Pérez A. Kinetics of chemical interesterification of sunflower oil with methyl acetate for biodiesel and triacetin production. *Chem Eng J* 2011;171:1324–32.
- [139] Casas A, Ramos MJ, Perez A. New trends in biodiesel production: chemical interesterification of sunflower oil with methyl acetate. *Biomass Bioenergy* 2011;35:1702–9.
- [140] Casas A, Ramos MJ, Pérez A. Methanol-enhanced chemical interesterification of sunflower oil with methyl acetate. *Fuel* 2013;106:869–72.
- [141] Modi MK, Reddy JRC, Rao B. Prasad RBN. Lipase-mediated conversion of vegetable oils into biodiesel using ethyl acetate as acyl acceptor. *Bioresour Technol* 2007;98:1260–4.
- [142] Kim SJ, Jung SM, Park YC, Park K. Lipase catalyzed transesterification of soybean oil using ethyl acetate, an alternative acyl acceptor. *Biotechnol Bioprocess Eng* 2007;12:441–5.
- [143] Jeong GT, Park DH. Synthesis of rapeseed biodiesel using short-chained alkyl acetates as acyl acceptor. *Appl Biochem Biotechnol* 2010;161:195–208.
- [144] Gonzalves VLC, Pinto BP, Silva JC, Mota CJA. Acetylation of glycerol catalyzed by different solid acids. *Catal Today* 2008;133–135:673–7.
- [145] Liao X, Zhua Y, Wang SG, Li Y. Producing triacetyl glycerol with glycerol by two steps: esterification and acetylation. *Fuel Process Technol* 2009;90:988–93.
- [146] Balaraju M, Nikhitha P, Jagadeeswarai K, Srilatha K, Sai Prasad PS, Lingaiah N. Acetylation of glycerol to synthesize bioadditives over niobic acid supported tungstophosphoric acid catalysts. *Fuel Process Technol* 2010;91:249–53.
- [147] Rezayat M, Ghaziaskar HS. Continuous synthesis of glycerol acetates in supercritical carbon dioxide using Amberlyst 15[®]. *Green Chem* 2009;11:710–5.
- [148] Galana MI, Bonet J, Sire R, Reneaume JM, Plesu AE. From residual to useful oil: revalorization of glycerine from the biodiesel synthesis. *Bioresour Technol* 2009;100:3775–8.
- [149] Bonet J, Costa J, Sire R, Reneaume JM, Plesu AE, Plesu V, Bozga G. Revalorization of glycerol: comestible oil from biodiesel synthesis. *Food Bioprod Process* 2009;87:171–8.
- [150] Ferreira P, Fonseca IM, Ramos AM, Vital J, Castanheiro JE. Acetylation of glycerol over heteropolyacids supported on activated carbon. *Catal Commun* 2011;12:573–6.
- [151] Casas A, Ruiz JR, Ramos MJ, Perez A. Effects of triacetin on biodiesel quality. *Energy Fuels* 2010;24:4481–9.
- [152] Rao PV, Rao BVA. Performance, emission and cylinder vibration studies of DI-diesel engine with COME-triacetin additive blends. *Int J Therm Technol* 2011;1:100–9.
- [153] Rao PV, Rao BVA, Radhakrishna D. Experimental analysis of DI diesel engine performance with triacetin blend fuels of oxygenated additive and COME biodiesel. *Iran J Energy Environ* 2012;3:109–17.
- [154] Li Y, Zhao X, Wang Y. Synthesis of dimethyl carbonate from methanol, propylene oxide and carbon dioxide over KOH/4A molecular sieve catalyst. *Appl Catal A* 2005;279:205–8.
- [155] Fabbri D, Bevon V, Notari M, Rivetti F. Properties of a potential biofuel obtained from soybean oil by transmethylation with dimethyl carbonate. *Fuel* 2007;86:690–7.
- [156] Notari M, Rivetti F. Use of a mixture of esters of fatty acids as fuel or solvent. Patent no. WO2004/052874 to Polimeri Europa; 2004.
- [157] Islam MR, Kurlle YM, Gossage JL, Benson TJ. Kinetics of triazabicyclodecane-catalyzed canola oil conversion to glycerol-free biofuel using dimethyl carbonate. *Energy Fuels* 2013;27:1564–9.
- [158] Kurlle YM, Islam MR, Benson TJ. Process development and simulation of glycerol-free biofuel from canola oil and dimethyl carbonate. *Fuel Process Technol* 2013;114:49–57.
- [159] Zhang L, Sheng B, Xin Z, Liu Q, Sun S. Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of homogeneous base catalyst. *Bioresour Technol* 2010;101:8144–50.
- [160] Panchal BM, Dhoot SB, Deshmukh SA, Sharma MR, Kachole MS. Production of DMC-BioD from *Pongamia pinnata* seed oil using dimethyl carbonate. *Fuel* 2013;109:201–5.
- [161] Ilham Z, Saka S. Dimethyl carbonate as potential reactant in non-catalytic biodiesel production by supercritical method. *Bioresour Technol* 2009;100:1793–6.
- [162] Ilham Z, Saka S. Production of biodiesel with glycerol carbonate by non-catalytic supercritical dimethyl carbonate. *Lipid Technol* 2011;23:10–3.
- [163] Tan KT, Lee KT. A review on supercritical fluids (SCF) technology in sustainable biodiesel production: potential and challenges. *Renewable Sustainable Energy Rev* 2011;15:2452–6.
- [164] Ilham Z, Saka S. Optimization of supercritical dimethyl carbonate method for biodiesel production. *Fuel* 2012;97:670–7.
- [165] Ilham Z, Saka S. Two-step supercritical dimethyl carbonate method for biodiesel production from *Jatropha curcas* oil. *Bioresour Technol* 2010;101:2735–40.
- [166] Su E, You P, Wei D. In situ lipase-catalyzed reactive extraction of oilseeds with short-chained dialkyl carbonates for biodiesel production. *Bioresour Technol* 2009;100:5813–7.
- [167] Zhang L, Sun S, Xin Z, Sheng B, Liu Q. Synthesis and component confirmation of biodiesel from palm oil and dimethyl carbonate catalyzed by immobilized-lipase in solvent-free system. *Fuel* 2010;89:3960–5.
- [168] Min JY, Lee EY. Lipase-catalyzed simultaneous biosynthesis of biodiesel and glycerol carbonate from corn oil in dimethyl carbonate. *Biotechnol Lett* 2011;33:1789–96.
- [169] Sun S, Zhang L, Meng X, Xin Z. Kinetic study on lipase catalyzed transesterification of palm oil and dimethyl carbonate for biodiesel production. *J Renewable Sustainable Energy* 2013;5:033127.
- [170] Wang Y, Cao X. Enzymatic synthesis of fatty acid ethyl esters by utilizing camellia oil soapstocks and diethyl carbonate. *Bioresour Technol* 2011;102:10173–40.
- [171] Su E, Du L, Gong X, Wang P. Lipase-catalyzed irreversible transesterification of *Jatropha Curcas* L. seed oil to fatty acid esters: an optimization study. *J Am Oil Chem Soc* 2011;88:793–800.
- [172] Awang R, May CY. Enzymatic synthesis of palm alkyl ester using dialkyl carbonate as an alkyl donors. *Am J Appl Sci* 2010;7:1083–6.
- [173] Zhang KP, Lai JQ, Huang ZL, Yang Z. Penicillium expansum lipase-catalyzed production of biodiesel in ionic liquids. *Bioresour Technol* 2011;102:2767–72.
- [174] Su EZ, Zhang MJ, Zhang JG, Gao JF, Wei DZ. Lipase-catalyzed irreversible transesterification of vegetable oils for fatty acid methyl esters production with dimethyl carbonate as the acyl acceptor. *Biochem Eng J* 2007;36:167–73.
- [175] Ansari FT, Choube A. Impact of biofuel in petrol engine—a review. *Int J Therm Technol* 2012;2:171–5.
- [176] Rounce P, Tsolakis A, Leung P, York APE. Comparison of diesel and biodiesel emissions using dimethyl carbonate as an oxygenated additive. *Energy Fuels* 2010;24:4812–9.
- [177] Li J, Wang T. Coupling reaction and azeotropic distillation for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate. *Chem Eng Process* 2010;49:530–5.
- [178] Ochoa-Gómez JR, Gómez-Jiménez-Aberasturi O, Maestro-Madurga B, Pesquera-Rodríguez A, Ramírez-López C, Lorenzo-Ibarreta L, Torrecilla-Soria J, Villarín-Velasco MC. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate by transesterification: catalyst screening and reaction optimization. *Appl Catal A: Gen* 2009;366:315–24.
- [179] Jaeger-Voirol A, Durand I, Hillion G, Delfort B, Montagne X. Glycerin for new biodiesel formulation. *Oil Gas Sci Technol—Rev IFP* 2008;63:395–404.
- [180] Pagliaro M, Ciriminna R, Kimura H, Rossi M, Pina CD. From glycerol to value-added products. *Angew Chem Int Ed* 2007;46:4434–40.
- [181] Caballero V, Bautista FM, Campelo JM, Luna D, Marinas JM, Romero AA, Hidalgo JM, Luque R, Macario A, Giordano G. Sustainable preparation of a novel glycerol-free biofuel by using pig pancreatic lipase: partial 1,3-regiospecific alcoholysis of sunflower oil. *Process Biochem* 2009;44:334–42.
- [182] Verdugo C, Luque R, Luna D, Hidalgo JM, Posadillo A, Sancho E, Rodríguez S, Ferreira-Díaz S, Bautista FM, Romero AA. A comprehensive study of reaction parameters in the enzymatic production of novel biofuels integrating glycerol into their composition. *Bioresour Technol* 2010;101:6657–62.
- [183] Verdugo C, Luna D, Posadillo A, Sancho ED, Rodríguez S, Bautista FM, Luque R, Marinas JM, Romero AA. Production of a new second generation biodiesel with a low cost lipase derived from *Thermomyces lanuginosus*: optimization by response surface methodology. *Catal Today* 2011;167:107–12.
- [184] Luna D, Posadillo A, Caballero V, Verdugo C, Bautista FM, Romero AA, Sancho ED, Luna C, Calero J. New biofuel integrating glycerol into its composition through the use of covalent immobilized pig pancreatic lipase. *Int J Mol Sci* 2012;13:10091–112.
- [185] Luna D, Bautista FM, Caballero V, Campelo JM, Marinas JM, Romero AA. Method for producing biodiesel using porcine pancreatic lipase as an enzymatic catalyst. European Patent EP 2 050 823 A1; 2009.
- [186] Luna C, Sancho ED, Luna D, Caballero V, Calero J, Posadillo A, Verdugo C, Bautista FM, Romero AA. Biofuel that keeps glycerol as monoglyceride by 1,3-

- selective ethanolysis with pig pancreatic lipase covalently immobilized on AlPO_4 support. *Energies* 2013;6:3879–900.
- [187] Wadumesthrige K, Ara M, Salley SO, Ng KYS. Investigation of lubricity characteristics of biodiesel in petroleum and synthetic fuel. *Energy Fuels* 2009;23:2229–34.
- [188] Xu Y, Wnag Q, Hu X, Li C, Zhu X. Characterization of the lubricity of bio-oil/diesel fuel blends by high frequency reciprocating test rig. *Energy* 2010;35:283–7.
- [189] Haseeb ASMA, Sia SY, Fazal MA, Masjuki HH. Effect of temperature on tribological properties of palm biodiesel. *Energy* 2010;35:1460–4.
- [190] Çelikten I. The effect of biodiesel, ethanol and diesel fuel blends on the performance and exhaust emissions in a DI diesel engine. *Gazi Univ J Sci* 2011;24:341–6.
- [191] Cheenkachorn K, Fungtammasan B. Biodiesel as an additive for diesohol. *Intern. J Green Energy* 2009;6:57–72.
- [192] Jaganjac M, Prah IO, Cipak A, Cindric M, Mrakovcic L, Tatzber F, Ilincic P, Rukavina V, Spehar B, Vukovic JP, Telen S, Uchida K, Lulic Z, Zarkovic N. Effects of bioreactive acrolein from automotive exhaust gases on human cells in vitro. *Environ Toxicol* 2011;27:644–52.
- [193] Pang X, Mu Y, Yuan J, He H. Carbonyl emission from ethanol-blended gasoline and biodiesel–ethanol–diesel used in engines. *Atmos Environ* 2008;42:1349–58.
- [194] Bhale PV, Deshpande NV, Thombre SB. Improving the low temperature properties of biodiesel fuel. *Renewable Energy* 2009;34:794–800.
- [195] Lapuerta M, García-Contreras R, Agudelo JR. Lubricity of ethanol–biodiesel diesel fuel blends. *Energy Fuels* 2010;24:1374–9.
- [196] Ribeiro NM, Pinto AC, Quintella CM, Rocha GO, Teixeira LSG, Guarieiro LLN, Rangel MC, Veloso MCC, Rezende MJC, Cruz RS, Oliveira AM, Torres EA, Andrade JB. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: a review. *Energy Fuels* 2007;21:2433–45.
- [197] Dunn RO. Effects of monoacylglycerols on the cold flow properties of biodiesel. *J Am Oil Chem Soc* 2012;89:1509–20.
- [198] Tang H, Salley SO, Ng KYS. Fuel properties and precipitate formation at low temperature in soy-, cottonseed-, and poultry fat-based biodiesel blends. *Fuel* 2008;87:3006–17.
- [199] Tang H, Guzman RD, Ng KYS. Comparing process efficiency in reducing steryl glucosides in biodiesel. *J Am Oil Chem Soc* 2010;87:337–45.
- [200] Dunn RO. Effects of minor constituents on cold flow properties and performance of biodiesel. *Prog Energy Combust Sci* 2009;35:481–9.
- [201] Echim C, Maes J, Greyt WD. Improvement of cold filter plugging point of biodiesel from alternative feedstocks. *Fuel* 2012;93:642–8.